REFINER
AND NATURAL GASOLINE MANUFACTURER
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Oil Steps Forward

INCREASED prices for petroleum are a move to test the ability of an industry to set its course in a desirable direction. Quotations existing prior to April 1 were such that no division of the industry could operate profitably. Now crude oil prices around the dollar mark, a figure which producers have pleaded for months. Finished materials have moved upward.

Viewed in the light of what the industry knows as potential supplies, these price advances were not justified. It has been known over a long period, however, that potential supplies and actual material are not identical. Since conditions to not permit the opening of oil fields to test output, even actual production is not known.

Through cooperative effort and statutory regulations output and consumption have been brought into balance. Proration has been in practice so long that it has become an accepted condition. Seldom is the question of the raising of proration heard. It is so remote that it is infrequently considered.

Under this situation the day of price increases from economic adjustments is far away. By holding output and consumption in balance, prices of products remain stationary and the prices existing did not allow a profit. The prospect was for continued operation at a loss until normal depletion of oil reserves brought demand ahead of supply.

This undesirable condition has been disrupted by a price increase for the deliberate purpose of jerking an industry into profit-making tempo ahead of the workings of economic factors. Hope rules on one side of this move; fear on the other. Certainly profit is the legitimate reward of endeavor. The fear comes from those of less optimistic temper as well as from those who have witnessed disaster from efforts to move faster than economics dictate.

If the oil industry can use its own boot straps to rise to a higher level of prices, it will have contributed materially to the economic plight of the country. Prosperity for the oil industry would rejuvenate a vast geographical district. The influence of oil on the Southwest is stupendous. Given a condition under which oil can be produced at a profit and a bulwark of buying power will be generated in an area of 22,000,000 population.

If refined products can be sold at a profit the nation over at least one industry will soon set itself aright. Its buying power soon would be felt through industry in general.

Success from this venture would become contagious. Other floundering industries might take heart and so adjust output and consumption that it would allow price advances into profitable ground.

Technological Unemployment

WHENEVER a product sells consistently below its cost of manufacture it is high time for its sponsors to peer into the future. Such is the position of natural gasoline, whose current market is little short of pitiful. It requires no extensive use of the pencil to justify the decision that this product can not long endure at prices around two cents a gallon. Even the moderate increases of recent weeks leave natural gasoline far below prices that will defray costs of manufacture.

Exact costs are not readily given. But the popular impression is that four cents a gallon is essential for natural gasoline if all costs are to be met. And this does not allow a profit.

The plight of natural gasoline differs from other petroleum products. Refinery gasoline has been selling below cost. But there is hope for this product, as it has been depressed by excessive still output. Once refinery throughput is put in balance, finished motor fuel will respond to a satisfactory price.

But natural gasoline is meeting what the economists refer to as "technological unemployment." Improved refining processes are calling for diminishing amounts of natural gasoline. Gasoline reforming units in particular have struck a hard blow at natural gasoline. As these are added to existing refining plants, the need for natural gasoline diminishes. This drag on natural gaso-

line promises to become more pronounced, for the trend is toward building more of these reforming units.

Natural gasoline is a worthy product. It has characteristics which stamp it as indispensable. But it no longer can be made under the assurance that refinery operation will consume unlimited output.

The campaign to establish natural gasoline is several years old. Outstanding developments have come about in this period. But it has never been the lot of this product to segregate itself from the refinery. The path always has led to the refinery. Now these paths are being closed.

The threat hangs over the smaller plants, those without facilities for stabilizing output and turning out finished products.

Of late there have been instances of the manufacture of solvents from natural gasoline. Liquefied gas is another product of the natural gasoline plant. But these are not sufficient to overcome the trend in petroleum refining. Still other avenues of use must be uncovered to offset the determination of refinery technicians to continue cracking gasoline until it is built in a desired motor fuel, rather than building the finished motor fuel through the addition of natural gasoline.

Tax Payers Win

OMISSION of the one-cent gasoline tax from the measure by which the budget of the United States was balanced late in March is a clean cut victory for the American automobile owner. It is true that the petroleum industry presented the facts and encouraged the voters to express themselves. But no man of the petroleum industry should look upon results as a triumph for the oil industry.

Had voters not expressed themselves as opposed to further levy on gasoline, that product would have been in the list along with cosmetics, automobiles and accessories.

The victory so far as petroleum is concerned lies in the fact that it has learned how to combat mounting gasoline taxes. The lesson is timely, for state legislatures will swing into action next year bent on still higher taxes. Gasoline tax rates of five, six and seven cents prevailing in some states is sufficient reason for asking for higher rates in states where rates are now three and four cents.

Tactics used successfully in avoiding a federal levy must be repeated wherever higher state taxes are proposed. First facts and figures must be presented to the legislature through its committees. Then the millions of automobile owners must be asked to voice their opinions. What they did at Washington is an example of what they will do in state capitols.

The man elected to office yields readily when his constituency speaks.

Less Outside Capital

THERE is some encouragement for industry in the drouth of "sucker" capital. Further expansion must come from earnings. Since earnings are trivial, industry will be content to operate its existing plant capacity.

Refining in particular has suffered from the sudden influx of this "sucker" capital. Only a year ago fresh money was drawn upon to build small refining plants under the promise that these plants would pay for themselves in three months. Some of those plants have not been operated three months.

Perhaps it has been unfortunate that in the past refining plants could be paid for within a short time. A few instances of quick return of investment followed by exorbitant profit were sufficient to draw fresh capital from sources unfamiliar with the oil industry.

It would seem now that such instances will not be cited again soon. The oil industry is striving like mad to avoid losses. If it does not have to combat fresh capital it will the sooner overcome losses.

Another commendable turn has been the attitude of established concerns toward the output of plants built to scalp a market. Not long back these plants soon had surplus supplies. Rather than see this material thrown on the market, established concerns bought it in what seemed like self defense.

Little of that buying takes place today. Overnight refining ventures have been turned away. It is true that their output put prices down, but they did not compel the industry to assume unreasonable stocks in a futile effort to save a market.

Code Under Fire

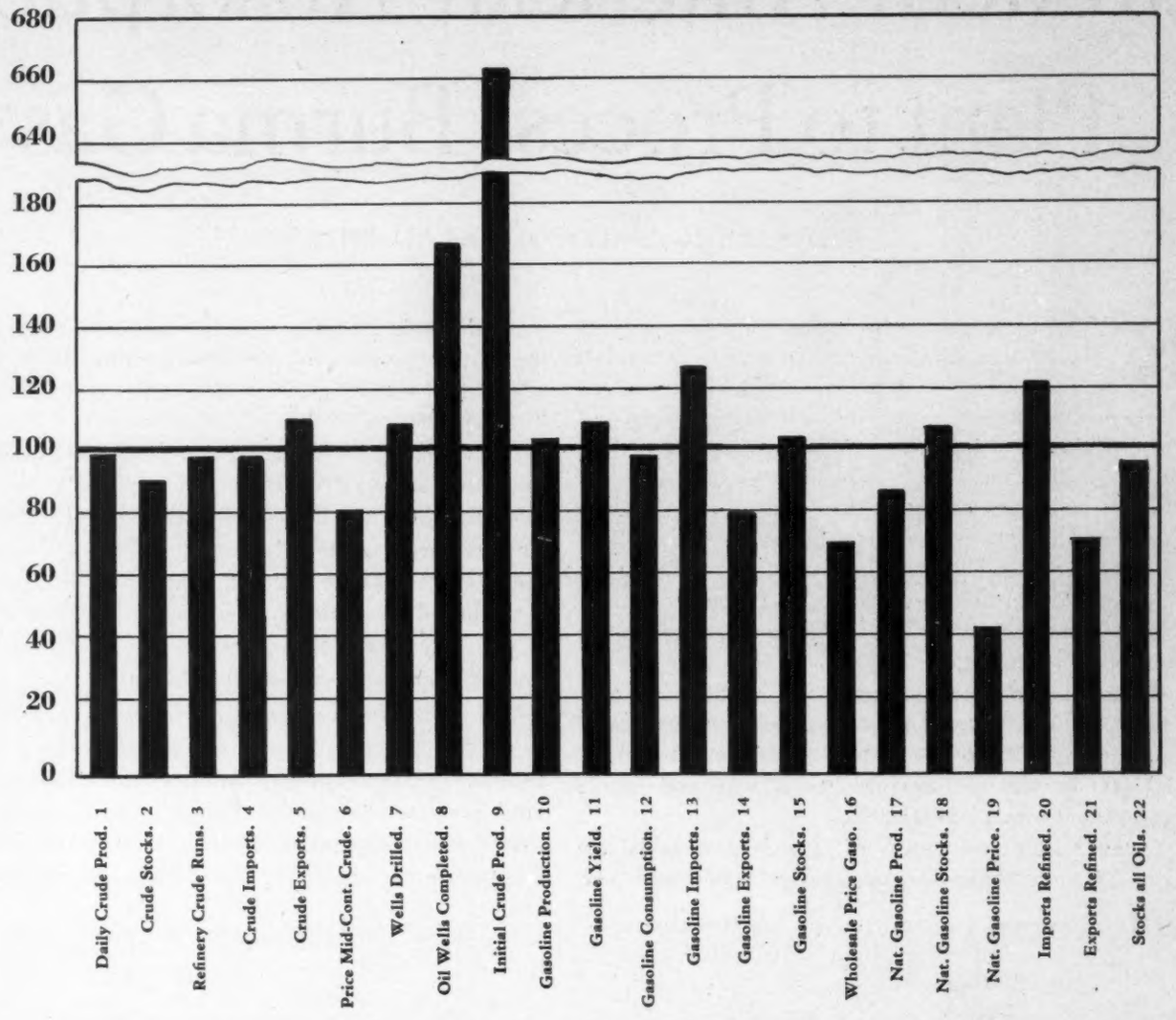
AFTER several weeks of preliminaries the petroleum industry is learning what its Texas litigation is all about. The attorney general of the Lone Star State filed a petition so broad in its accusations that it failed to mention particulars.

Now it seems that the National Code of Practices for the Marketing of Refined Petroleum Products is to be the kernel of the suit through which he will seek to collect more than $17,000,000 and cancel the charters of 15 large oil concerns. Maintaining business under the provisions of the Code is the offense against the State of Texas.

The irony of this is the condition under which the Code came into existence. Two representatives of the Federal Trade Commission sat in St. Louis to supervise the drafting of the Code. The Commission approved its rules. Later it rescinded this action but upon reconsideration redrafted the rules and again approved.

Now the elected official of one state would make this one reason for the collection of excessive fines and the cancellation of charters.

Salient Oil Industry Factors for February, 1932, Expressed in Per Cent of February, 1931. Heavy Line (100) Represents February, 1931



Oil Industry Barometer—February, 1932

Index of Salient Factors

	Factors—	February 1931	February 1932	2 Months Ending February Index (1)	2 Months Ending February 1931	2 Months Ending February 1932	Index (1)
1	Daily Average Crude Production (Thous. Bbls.)	2166	2,155	99.4	2,142	2,156	100.6
2	Total Crude Stocks (Thous. Bbls.)	405,315	369,388	91.1	405,315	369,388	91.1
3	Refinery Crude Runs (Thous. Bbls.)	65,249	63,814	97.8	135,275	132,529	98.0
4	Crude Imports (Thous. Bbls.)	4,789	4,708	98.3	9,142	6,755	73.9
5	Crude Exports (Thous. Bbls.)	1,710	1,897	110.9	3,629	3,530	97.3
6	Posted Price 36 Gravity Mid-Cont. Crude (Per Bbl.)[2]	$.95	$.77	81.1	$.95	$.77	81.1
7	Wells Drilled	815	884	108.4	1,971	1,915	97.1
8	Oil Wells Completed	348	583	167.5	867	1,276	147.1
9	Initial Crude Production (Thous. Bbls.)	460	3,050	663.0	1,257	6,555	521.4
10	Gasoline Production (Thous. Bbls.)	31,328	31,764	101.4	64,036	65,299	101.2
11	Gasoline Yield—Average Per Cent of Crude[4]	42.49	46.03	108.3	41.87	45.26	108.0
12	Domestic Gasoline Consumption (Thous. Bbls.)	26,061	25,508	97.9	52,977	52,353	98.8
13	Gasoline Imports (Thous. Bbls.)	948	1,195	126.0	2,064	2,419	117.1
14	Gasoline Exports (Thous. Bbls.)	3,606	2,849	79.0	8,509	6,271	73.7
15	Gasoline Stocks at Refineries (Thous. Bbls.)	45,355	46,923	103.4	45,355	46,923	103.4
16	Refinery Price U. S. Motor Gaso.—Group 3 (Cents)[3]	4	2⅞	70.8	4⅛	3	72.7
17	Natural Gasoline Production (Thous. Bbls.)	3,631	3,148	86.6	7,771	6,490	83.5
18	Natural Gasoline Stocks (Thous. Bbls.)	3,288	3,508	106.7	3,288	3,508	106.7
19	Price Grade "A" Natural Gasoline, Group 3 (Cents)[3]	3¼	1⅜	42.3	3⅝	2¼	62.1
20	Imports of All Refined Oils (Thous. Bbls.)	2,917	3,536	121.2	6,518	7,086	108.7
21	Exports of All Refined Oils (Thous. Bbls.)	7,992	5,892	73.7	18,083	12,881	71.2
22	Total Stocks of All Oils (Thous. Bbls.)	658,380	633,128	96.2	658,380	633,128	96.2
	Weighted Index of Supply	.....	.....	103.0	.....	.....	98.2
	Weighted Index of Demand	.....	.....	91.8	.....	.....	87.8
	Weighted Index of Prices	.....	.....	64.7	.....	.....	71.9

[1]—Last Year—100.
[2]—Weighted Average. [3]—Monthly Average.
[4]—Straight run and cracked gasoline only.

See Additional Economics in Month in Review Section, Page 59a

Modern American Absorption Plant to Process Burma Gas

CHARLES H. SMITH and BRAD MILLS

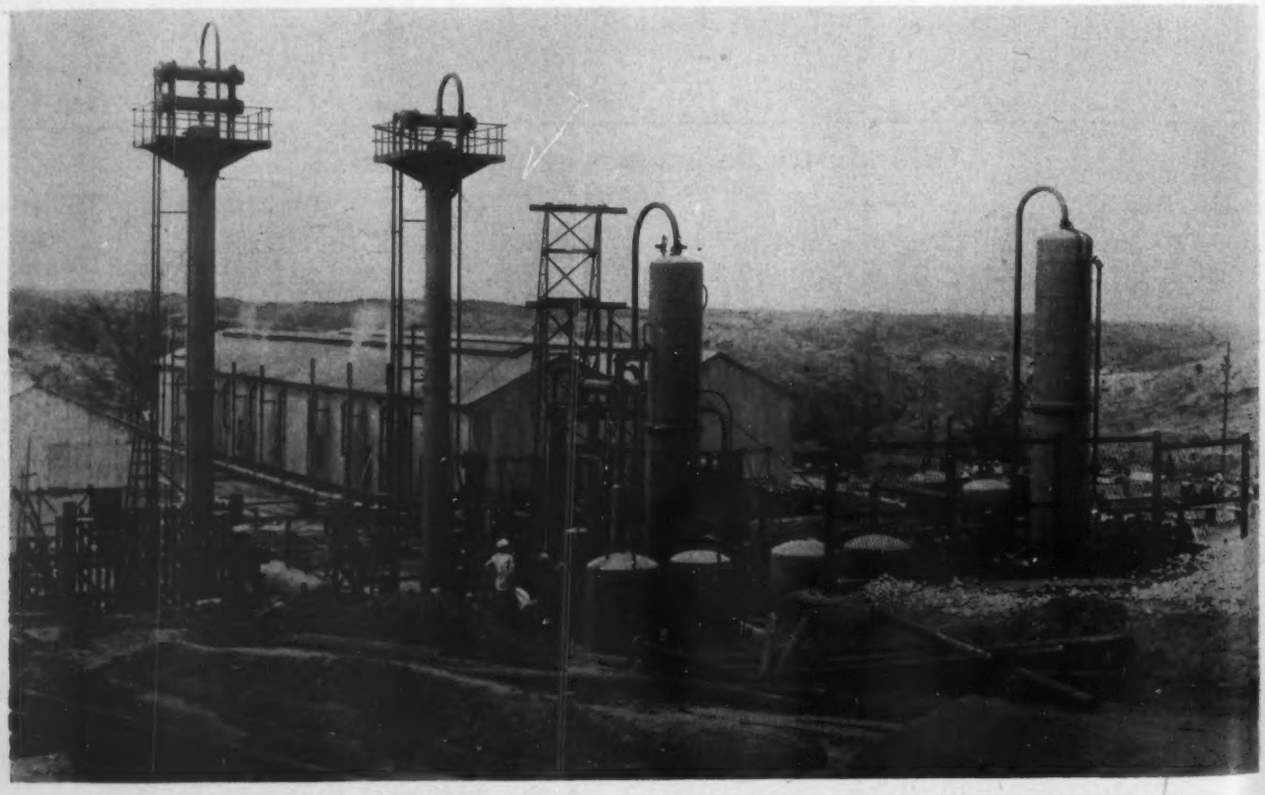
RECENT completion by Burmah Oil Company of two modern American absorption plants marked a trend toward gasoline extraction from gas which had been used extensively for repressuring and other purposes. Conditions for the manufacture of natural gasoline on a large scale were long regarded as favorable, but development of the necessary equipment was a considerable task, due to the remoteness of Burma's oil fields and the expense involved. Equipment manufactured in the United States was selected in competition with that which might have been assembled from other countries.

Burma's oil industry is second only to rice in importance. Annual export of petroleum products consists of approximately 3,000,000 barrels of kerosene; about 2,500,000 barrels of gasoline; and a wax and candle trade valued around $4,000,000.

YenangYaung and Singu, the two largest fields, are about 300 miles above Rangoon on the Irrawaddy River. They lie about 50 miles apart. Owned and controlled by the British government, the fields produce under supervision of a warden, who is also the civil magistrate of the field district.

Chief among the operating companies, is Burmah Oil Company, Limited, which has at Syriam, a few miles from Rangoon, the largest oil refinery in the Far East. This refinery treats oil from the YenangYaung and Singu fields. Three hundred miles of 10-inch pipe conveys the oil from fields to refinery. Incidentally, this is the only crude trunk line in all of Burma. The smaller companies ship entirely by barge.

The wells produce gas with the oil and repressuring is general practice. Thus, no gas is wasted, but no serious attempt at complete gasoline extraction occurred until early in 1931 when Burmah Oil Company purchased two absorption plants. One plant was for YenangYaung, the other for Singu. Both were de-



Burma Oil Company's Gasoline Plant at YenangYaung, Burma, showing double stabiliser at left, still and surge tanks in center, absorber and gas coolers at right.

signed, manufactured, completely installed, and started by C. F. Braun & Company.

PLANT DESCRIPTION

Except for the stabilizers, the plants are duplicates. The major apparatus in the absorption and distillation units consists of:

Two 84-inch gas scrubbers.
One 84-inch 22-tray bubble-type absorber.
Three F-120 gas coolers.
Four I-155 lean-to-fat oil exchangers.
One 72-inch 18-tray Fractostill.
Four I-155 lean-oil coolers.
Two G-120 and 2-F-155 gasoline condensers.
Two G-120 fat-oil preheaters.

In addition, are the usual fat-and-lean-oil vent tanks, dehydrators, and gasoline accumulators. All heat-exchangers, condensers, and coolers carry by-pass valves to facilitate cleaning, and increase plant flexibility.

The stabilizer at the YenangYaung plant is a double unit. Principal equipment includes:

Two 32-inch 22-tray columns;
Four reflux condensers;
Two reboilers;
Two heat exchangers;
Two preheaters;
Two coolers;
Two final condensers.

Operation of the complete unit produces a commercial gasoline, and a light gasoline; operation of one column only, produces stabilized natural gasoline.

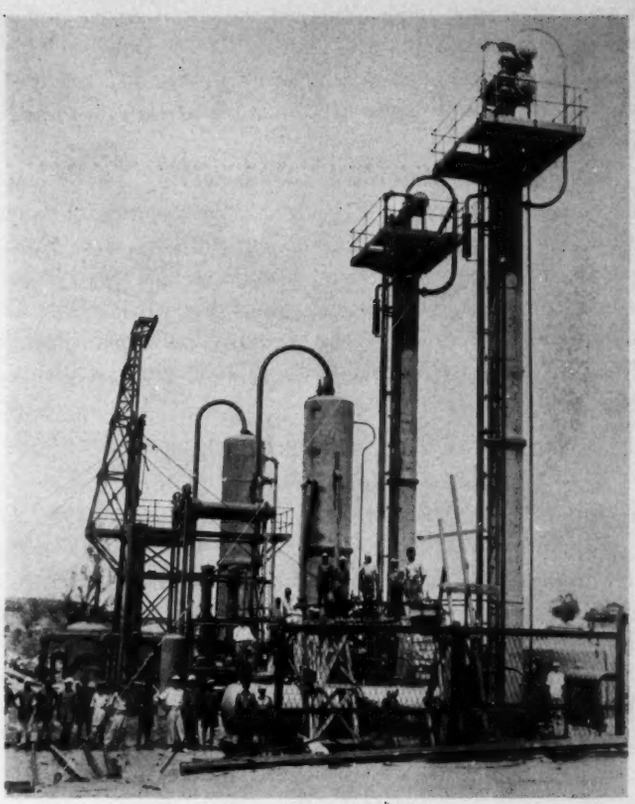
The Singu stabilizer makes natural gasoline only. Its major equipment is: a 32-inch 22-tray column, two reflux condensers, one reboiler, two heat exchangers, two coolers, a preheater, and the usual tankage. The plant arrangement provides for the addition of a second column later, if needed.

A ventilating-louver cooling tower at each plant cools all water used in coolers and condensers. The towers are identical; each is 90 feet long by 19 feet wide by 44 feet high. Spray distributors improve cooling, and provide uniform distribution over the cross-section.

Each plant also includes a 190 horsepower Ingersoll-Rand gas-driven recompressor for recovery of the vent vapors. Intercoolers and aftercoolers are provided.

Pump units for the absorption plant are very compact. Pumps for water, lean-oil, fat-oil, and reflux are DeLaval centrifugals, all on one shaft, driven by a 200 horsepower General Electric motor. A special motor winding combats the high humidity and high atmospheric temperature. An identical pump unit acts as a standby. Burmah Oil Company makes its own electricity in a central station at Nyaunghla. All established drilling and pumping operations are electrified. Stabilizer charging and reflux pumps are Dean Brothers simplex single acting. These are steam driven.

Neilan liquid-level controllers; Tycos temperature-recorders and pressure-recorders; Crosby safety-valves and pressure gages; Fisher and Paracoil traps; and Penberthy gage cocks and glasses comprise the instrumentation.



All condensers are reflux condensers are shell-and-tube type. Parallel connected units permit cleaning without complete plant shut down

CONSTRUCTION

Good facilities for construction do not exist. Much of the preliminary work utilizes primitive methods. Excavation, for instance, is entirely by coolie labor. These men break the dirt into small lumps with picks and mattocks, pack it into large, flat baskets, and carry the baskets on their heads to disposal. Similarly, concrete is hand-mixed by men, and carried to the forms by women. Immense "dish-pans" replace wheelbarrows or conveyors. The absence of labor-saving machines indicates no lack of progressiveness; it shows, instead, a real effort towards unemployment relief.

There are no gravel deposits. Rock for concrete, is hauled by the men in bullock-carts from the surrounding countryside. The large rocks, (much of it is petrified wood), are deposited in a village. Here, the women and children break the rock with small hammers. Again bullock-carts transport it to the site. Then it is hand-cleaned and sorted.

Streams supply the sand, and again bullock-carts furnish the transportation.

Form-work is all of jungle wood almost too hard for nailing. The accurate form-work is constructed by Chinese carpenters in shops. Instead of nails, holes are drilled and wood screws used. Box forms are mortise-tennon and key.

Lacking reinforcing steel, half-inch round band-iron

was used. Spot welds replaced the usual wire tying in order to secure a bond. The actual erection, and mechanical assembly entailed no serious difficulty, and proceeded rapidly in spite of a complete lack of skilled mechanics.

Native labor performed all the work. There were Indians of various castes; some Chittagonians; some Burmese; and others Chinese. Supervisors were Europeans. The only American was E. L. Varney, Braun construction engineer, in charge of the work. The accompanying pictures of the YenangYuang plant, taken by an itinerant Chinese photographer, give an idea of the type of workmen.

OPERATION

The YenangYaung plant started operation early in October, 1931. Tests were made at various loads. Initial gas quantities varied from 7,000,000 to 12,500,000 cubic feet daily. Later, quantities up to 17,000,000 cubic feet daily passed through the plant. Gasoline content varied from 1.5 to 1.7 gallons per thousand cubic feet.

Oil circulations varied from 320,000 to 490,000 gallons per day. At first, the only oil available was a low-initial distillate. This prevented operation at low oil-circulations, as vapor binding occurred in pump cases when the discharges were throttled. A later replacement of the oil corrected this difficulty. With the initial oil-gas ratios, 100 per cent butane extraction obtained. Later operation reduced this percentage to American practice.

PRODUCTS

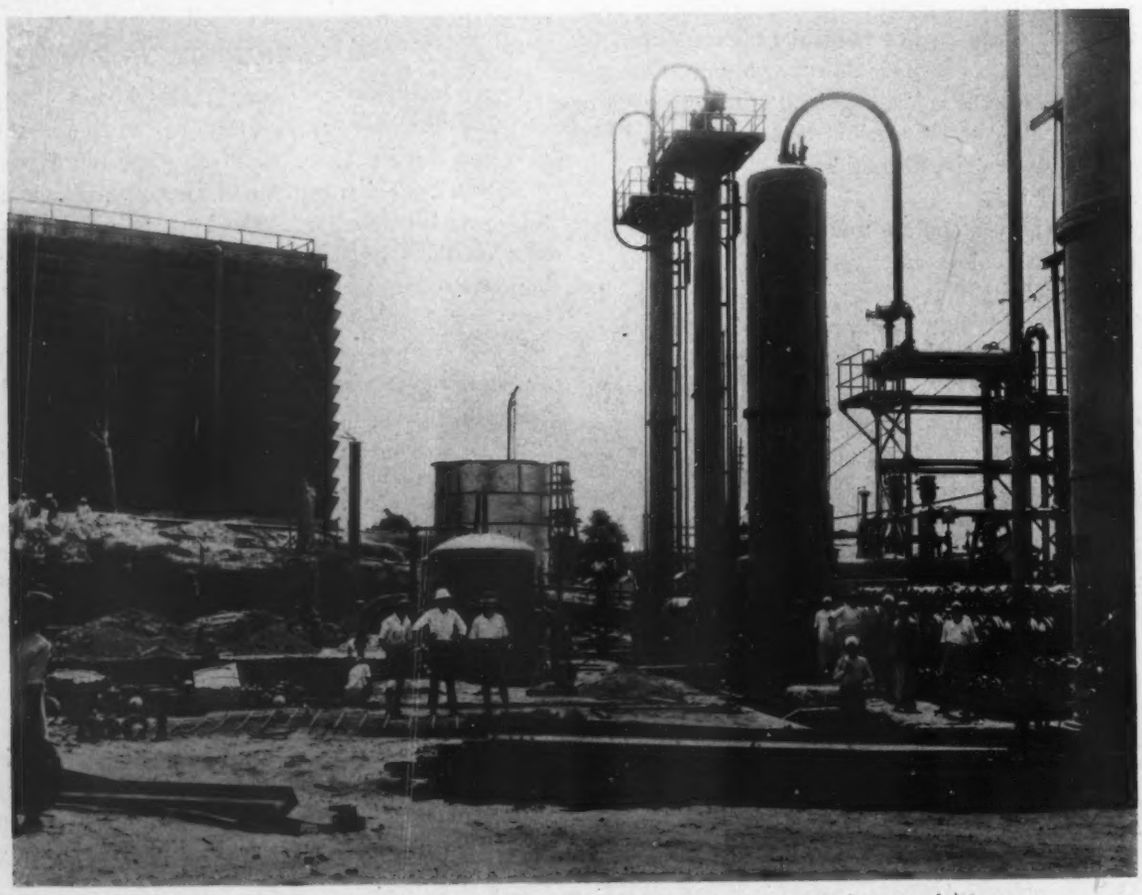
Original specifications on the double stabilizer gave a feed of 85-90° A.P.I. natural gasoline. Products required were: a marketable gasoline with I.B.P. 100° F., gravity 70° A.P.I., and vapor pressure 8 lb./sq. in. absolute at 100° F.; and a light gasoline sp. gr. 0.6, and vapor pressure 40 lb./sq. in. absolute at 100° F.

Preliminary operation produced these, and several other products. After some experimentation, Burmah Oil Company decided to make the commercial gasoline of 62-30° A.P.I. with the same vapor pressure as before. The initial point increased a few degrees.

When operated as described, the YenangYaung plant produces enough marketable gasoline in one week to supply all of upper Burma for a month. So the remaining three weeks, the secondary column is inactive, and the primary column supplies a stable natural gasoline with 18 lb./sq. in. absolute vapor pressure at 100° F. This flows with the crude to the refinery.

The light gasoline resulting from the double-unit operation flows to pressure storage at the plant. From here, small quantities blend with the natural gasoline in the crude lines for transportation. It is impossible to blend in large quantities because of atmospheric storage en route.

Full load operation of the two plants will recover nearly 45,000 gallons of stable natural gasoline daily. This maximum is a future figure, as the gas load at Singu is now light.



Control-way, showing gage boards, jump pit and the ventilating louvre cooling tower.

Cracking Characteristics of East Texas Crude

A. W. TRUSTY and A. C. HOLDER
Louisiana Oil Refining Corporation,
Shreveport, Louisiana

THE importance of the supply of East Texas residuum as a cracking stock has been realized by the oil industry. The large supply of crude from this field, conservatively estimated at 1,250,000,000 barrels of potential production, together with the fact that the sale of the residuum as fuel oil is limited due to its extremely high pour test, demand that the oil be cracked in order to dispose of the large amount of residuum. Laboratory cracking tests have been made to determine the relative cracking tendencies, the relative gas losses, and anti-knock characteristics of the various fractions from East Texas crude.

DESCRIPTION OF APPARATUS

The feed tanks were two liter graduated cylinders. A coil one-quarter inch by 12 feet and heated by means of an electric heater was used as a preheater. The preheater was connected directly into three feet of three-quarter inch pipe which was heated by means of electric furnaces. A recording pyrometer was used for temperature measurement. The coil outlet was connected to a brass condenser. The cracked oil was received in a flask and the gas was scrubbed in a glass column packed with glass beads before being vented to the air. The feed stock was forced into the system by means of gas pressure. No fractionation was used on the still due to the small volume of oil handled. The operating conditions were

Preheater Temperature.....700°F.
Coil Outlet Temperature.....1080°F.
Rate of Throughput.....8 c.c./minute
Pressure on system.....
.....Less than 1 lb. gauge

FEED STOCKS USED

One barrel of East Texas crude was distilled, taking the gas oil cuts off under 25-inch vacuum in order to prevent incipient cracking. Ten overhead fractions were taken ranging from heavy naphtha to heavy gas oil. Tests are shown on each cut.

Sachaneu and Tilicheyev have shown that the rate of

Original Fractions from Gregg County Crude Before Cracking

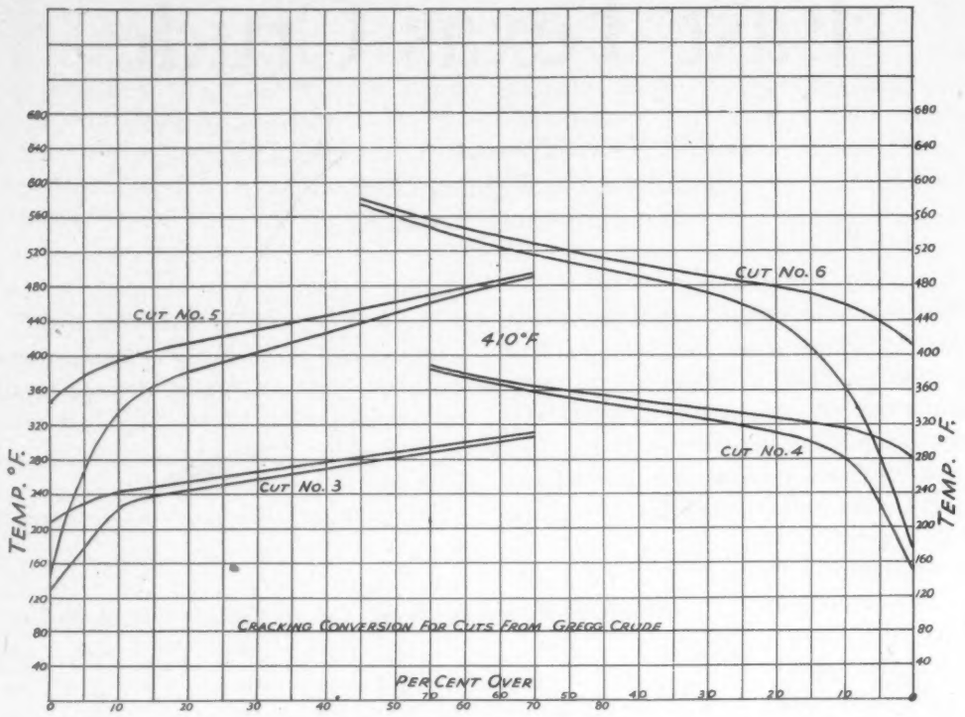
	Cut No. 1	Cut No. 2	Cut No. 3	Cut No. 4	Cut No. 5	Cut No. 6	Cut No. 7	Cut No. 8	Cut No. 9	Cut No. 10
Gravity . ..	71.4	61.2	52.6	46.3	40.1	36.8	33.7	30.8	28.5	30.7
I. B. P. ...	96	160	206	284	346	414	454	430	364	270
10%	116	190	242	314	396	460	516	584	650	422
20	128	197	252	326	414	477	534	612	692	522
30	140	204	264	334	428	490	550	627	...	606
40	150	210	274	346	444	504	565	642	...	668
50	164	220	287	358	460	520	584	657	...	...
60	180	228	300	370	477	536	604	...	...	...
70	198	238	315	388	497	556	623	...	...	...
80	232	258	332	406	520	580	...	...	...	...
90	260	284	362	436	568	621	...	...	...	...
95	288	312	392	462	616	...	...	...	...	...
End Point .	324	370	450	488	634	...	...	...	...	...
% at 122°F.	14.5	...	...	...	...	...	...	...	...	...
% at 158...	47.5	...	...	...	...	...	...	...	...	...
% at 212...	74.5	41.5	01.0	...	...	...	...	...	...	...
% at 221...	77.0	52.0	02.0	...	...	...	...	...	...	...
% at 284...	94.0	90.0	48.0	...	...	...	...	...	...	...
% at 392... ..		..	95.0	...	...	...	...	...	...	...
% at 410... ..		..	97.0	81.0	15.5	...	...	...	01.0	06.5
% at 650... ..		..	..	...	...	94.0	79.0	49.0	10.0	37.0
Carbon Residue... ..		..	.005	.01	.01	.01	.015	.02	.09	.16
Aniline No.	133	128	126	132	147	159	168	178	188	175

Note: Cut Number 10 cracked during the topping operation due to failure of the vacuum pump. The normal aniline number is about 185°F. for this cut.

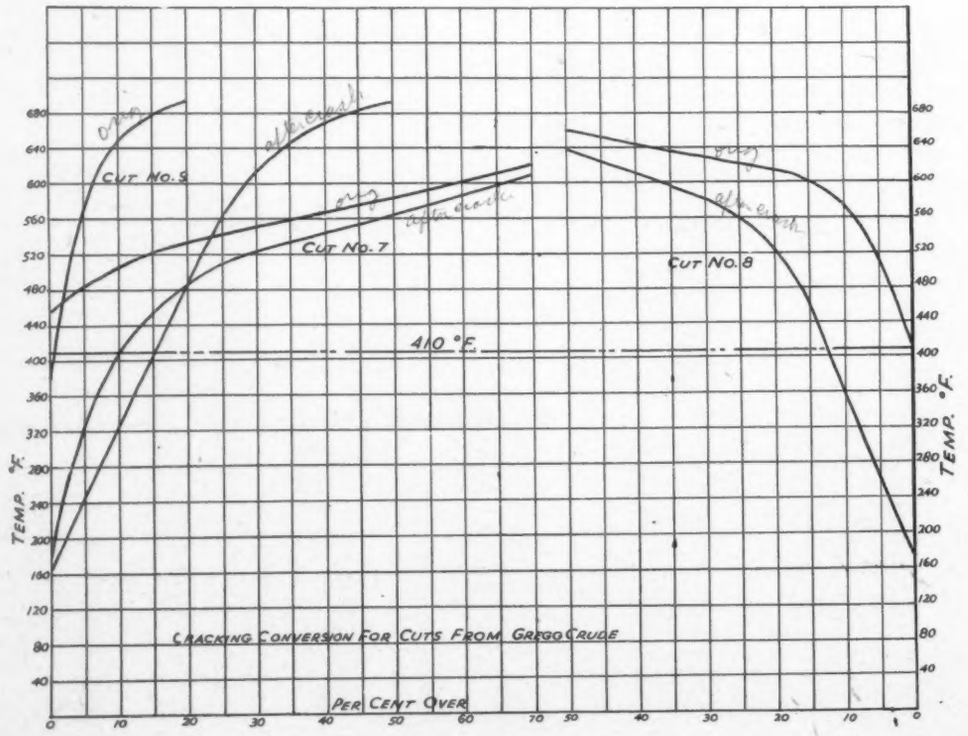
Fractions from Gregg Crude After Cracking

	Cut No. 2	Cut No. 3	Cut No. 4	Cut No. 5	Cut No. 6	Cut No. 7	Cut No. 8	Cut No. 9	Cut No. 10
Gravity	61.5	53.1	47.2	41.3	37.9	35.2	32.5	29.6	32.1
I. B. P.	130	130	146	142	146	176	166	162	185
10% at	182	228	284	342	366	410	360	328	324
20	192	246	312	380	440	488	530	490	410
30	202	258	326	414	470	524	584	618	498
40	209	270	342	430	490	544	614	668	562
50	218	280	354	448	506	566	638	693	632
60	226	294	366	468	526	586	656	...	...
70	236	311	384	488	546	606	682	...	...
80	248	326	406	512	578	640	...	...	...
90	284	362	442	556	622	684	...	...	...
95	314	400	486	608	...	...	...	...	...
End Point	374	460	524	630	676	...	...	...	...
% at 410		95.5	81.0	28.0	15.0	10.0	11.5	14.0	20.0
Aniline Number ..	118	113	117	133	135.5	145.5	152	144	134
Decrease in Aniline No. due to crk...	10	13	15	14	23.5	22.5	26	44	41

Cracking Conversion for Cuts from Gregg Crude



Fractions 3, 4, 5 and 6



Fractions 7, 8 and 9

cracking is a function of the boiling range of the cracking stock. Light gas oil takes nearly twice as long to crack as heavy fuel oil and kerosene is five times as slow as gas oil. These relative susceptibilities to cracking are shown in the above ultimate yields: the gas oil fractions, cuts Number 7 and Number 8 show considerable more gasoline conversion than do cuts Numbers 3, 4 and 5. By comparison of the curves showing cracking conversion, it is noted that the heavy gas oil is changed throughout the entire range of its boiling range, in fact, with cuts Numbers 8, 9 and 10 there is more conversion of the hydrocarbons boiling from 410°F. to 650°F. than of the hydrocarbons boiling under 410°F.; whereas with cuts Numbers 3, 4 and 5 there is comparatively more conversion of the hydrocarbons boiling under 410°F. than of the higher boiling hydrocarbons. The aniline numbers on the bottoms from cuts Numbers 7, 8, 9, 10 show also that there was conversion for these fractions.

The high gasoline conversion shown for cut Number 5, which at first looks inconsistent, can be explained by the fact that this fraction is very rich in hydrocarbons boiling immediately under and over 410°F., and during cracking, a large proportion of the hydrocarbons boiling slightly above 410°F. are "reformed" sufficiently to cause them to boil below 410°F. and actually show an abnormal gasoline conversion. However, the aniline number on cut Number 5 before and after cracking shows that the actual hydrocarbon conversion was no higher than its relative position in boiling range scale should indicate. The distillation range of the gasoline also indicates that the gasoline is composed of heavy hydrocarbons.

The anti-knock value decreases as the heavier fractions are cracked. The knock rating on the gasoline produced from cracking a paraffin fraction is much poorer than the knock rating on the gasoline produced from cracking a naphthenic fraction. As shown by the aniline numbers and by the pour test, the light gas oil fractions contain more naphthenic hydrocarbons than do the heavy gas oil fractions, which explains the lower antiknock value of the gasolines from the heaviest gas oil cuts.

Fractions from Gregg Crude After Cracking

The cracked oil was charged into a three-liter flask and distilled through a Hempel fractionating column to determine the yield of gasoline. Tests are shown on the gasolines from each cracked fraction:

Gasoline from	Cut No. 3	Cut No. 4	Cut No. 5	Cut No. 6	Cut No. 7	Cut No. 8	Cut No. 9	Cut No. 10
Gravity	52.7	48.8	50.7	56.6	56.7	55.5	53.9	53.7
I. B. P.	170	146	115	114	115	108	110	114
10% at	229	268	168	164	162	157	168	172
20	244	288	226	184	182	182	193	200
30	255	300	260	203	200	204	215	225
40	266	314	284	221	221	220	238	248
50	276	322	304	239	244	256	266	262
60	286	328	324	259	266	282	288	294
70	300	342	336	280	288	307	312	312
80	319	354	349	307	312	333	338	334
90	342	372	368	350	342	363	365	358
95	362	390	386	377	390	384	388	392
End Point	390	410	412	414	404	410	408	410
% at 122°F.	..	...	1	1	1.5	1.5	1	1
% at 158	..	0.5	4.5	7	8.5	10.5	7	7
% at 212	5	3.0	16.0	35	36.5	36.0	28	25.5
% at 221	8	5.0	19.0	40	40.0	40.5	32	28.5
% at 284	57	18.0	40.0	73	67.0	61.0	58	55.0
% at 392	..	95.5	96.0	96.5	95.5	96.5	96	95.0
Recovery	98	98	98	98	98	98	98	98
Color	Yellow	Y.	Y.	Y.	Y.	Y.	Y.	Y.
Octane Number °F.	63	61	76	78	77.5	77	76	74

Octane Number of Natural Gasoline in Cuts No. 2, No. 3 and No. 4

	Before Cracking	After Cracking
Cut No. 2	63	63.5
Cut No. 3	50	63
Cut No. 4	46	61

Bottoms from Cracked Fractions from Gregg Crude After Cracked Gasoline Has Been Removed

Bottoms from—	Cut No. 3	Cut No. 4	Cut No. 5	Cut No. 6	Cut No. 7	Cut No. 8	Cut No. 9	Cut No. 10
Gravity	..	39.7	37.1	34.6	32.1	28.2	24.5	25.6
I. B. P.	..	386	408	410	442	498	482	430
10% at	..	408	422	454	504	570	587	500
20	..	415	434	468	524	598	650	544
30	..	420	446	482	540	617	678	596
40	..	425	455	502	556	636	700	650
50	..	430	467	516	573	656	...	...
60	..	437	480	532	590	672	...	...
70	..	447	496	552	610	690	...	...
80	..	465	520	583	640	...	...	...
90	..	494	560	630	688	...	...	...
End Point	..	574	648	...	...	...	...	...
Aniline No.	139	137	141	147	157	163	160	150

Comparison of Aniline Numbers

	Before Cracking	After Cracking	Bottoms of Cracked Fractions (Gasoline removed)
Cut No. 3	126°F.	113°F.	139°F.
Cut Number 4	132	117	137
Cut Number 5	147	133	141
Cut Number 6	159	135.5	147
Cut Number 7	168	145.5	157
Cut Number 8	178	152	163
Cut Number 9	188	144	150
Cut Number 10	175	134	150

Ultimate Yields

	Cut No. 2	Cut No. 3	Cut No. 4	Cut No. 5	Cut No. 6	Cut No. 7	Cut No. 8	Cut No. 9	Cut No. 10
Gasoline 405°F. E. P.	0	0	3.6	13.5	8.5	9.0	11.9	14.0	21.4
Gas Oil or Fuel Oil	0	91.0	91.9	79.5	83.5	82.0	78.1	75.0	65.6
Gas	1.5	3.0	4.5	7.0	8.0	9.0	10.0	11.0	13.0

Notes on Selective Fractionation

C. B. FAUGHT
Refining Engineer

WORKING on the theory that fractionation could be made selective so that each side stream would be finished material, requiring only chemical treatment, where necessary, a bubble tower such as is shown in the accompanying sketch, was designed and erected. Crude was being secured from several sources and it was necessary for the tower to cut products from the various crudes to meet the same general specifications.

In order to accomplish these results it was necessary to maintain the stripping sections at uniform temperatures regardless of throughput. This problem was solved through the use of a series of automatic reflux controllers and air actuated liquid level controllers.

As the tower heated up when starting the unit on its operating cycle, the reflux controllers were not used until the top of the tower reached its normal temperature. The side streams were then set at the desired temperatures, the automatic reflux valves were opened and the tower automatically balanced itself. The stripping sections consist of a box with an open top so that approximately 15 inches of liquid is maintained. The automatic level controller maintains the level so that sufficient material lays in the section to insure good stripping action from the open steam spray.

The initial boiling point of the side streams is maintained at the desired temperature by the amount of steam admitted. The end point of the streams is controlled by the reflux which enters just above the first tray below the stripping section. The initial boiling point of any side stream can be "gapped" several degrees with this tower, the amount of gap being determined by the volume of steam used.

In addition to its ability to automatically produce side streams to specifications, this tower design improves the quality of the side streams. It was found that in running an East Texas crude, a kerosene of 38.5 gravity was produced which was 30 plus in color; and this color was stable after storage for several months. The gas oil of 32-34 A. P. I. gravity was better than I — N. P. A. color.

This was due to the internal washing which the tower received. In addition to the knock back which is obtained in any bubble tower, the reflux used in each section—which is a portion of the stream which comes off of that section—travels downward from tray to tray, washing the heavier materials down so that no material lies dormant on any tray. This flushing action sweeps the trays clean, which helps the color of the streams. The gases passing up through the tower, receive a thorough washing on each tray and due to the cold reflux entering each stripping section, no material passes up out of the distillation range of the stream where it is condensed. This practice gives straight distillation curves.

In order to change the specifications of any side stream, it is necessary only to set the new temperature on the reflux controller and the tower adjusts itself. The amount of reflux is automatically adjusted.

This continuous washing inside of the tower decreases the polymerization which would otherwise occur in the trays. The material on the trays, when sluggish in its return to the take-off below, tend to polymerize under the heat required for processing. A certain amount of concentration of this polymerized material takes place, raising the end point of the stream below, artificially. This decreases the percentage of the stream of that material which is obtained from the crude, due to the raised end point, which is caused by such polymerization. This polymerized material causes a higher end point and lower gravity in the stream. Should this material be eliminated, more of the contents of the bubble tower could be taken out and still maintain the same end point on any given stream. This polymerization is especially noticeable in sour crudes.

Both gum and sulfur increased very rapidly in the gasoline when the end point was raised. A 400 end point gasoline could be taken off the top showing a gum content of 12 mg. and a sulfur of .13 per cent. Upon increasing the end point to 420, the gums would increase to 45 mg. and the sulfur to .25 per cent. It was found that adding internal reflux just below the section where a material of kerosene distillation range was being withdrawn, the sulfur on the overhead stream would drop from .02 to .03 per cent and the gums would decrease about one-third. This seemed to indicate that there

was considerable polymerization taking place in the tower due to heavy fractions rising into the section. Internal reflux in the kerosene section improved the color of that stream very materially. The distillation, however, proved that no light material was being taken out in the lower section.

These conclusions were based over a period of time. The fact that the sulfur on the gasoline stream was lowered is explained by the fact that sulfur compounds are found in all of the fractions of a sour crude, the sulfur compounds present in any fraction evidently conform in distillation range with the stream itself. Lowering the point at which these compounds were condensed, evidently was accomplished by means of control of fractionation.

METALLIC SODIUM

In connection with the removal of sulfur from sour crudes, other than by fractionation, experiments were conducted in which metallic sodium was used as the removing medium.

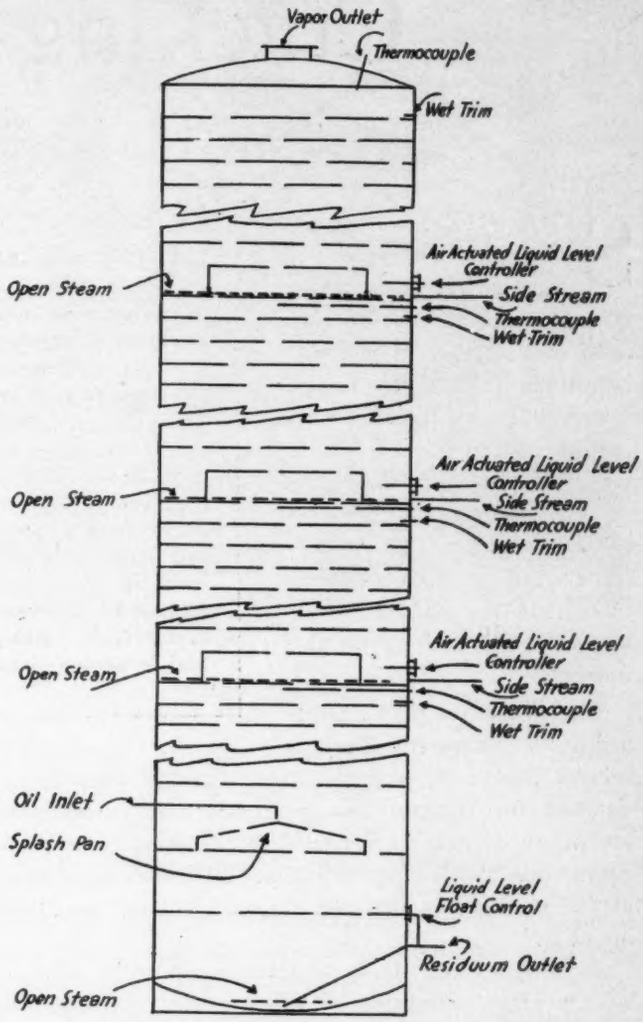
The application of the sodium was comparatively easy in glass. The gasoline is first washed entirely free of hydrogen sulfide and dried. It is then re-distilled and the vapors passed through a bath of sodium which had previously been liquefied and was being held at a temperature of 350° to 400° F. Sodium at this temperature is liquid. As the gasoline passed through the sodium, the sulfur compounds were all removed, leaving the resulting product free of sulfur and also free of gums. This gasoline was a brilliant white, stable to sunlight for many days. The reaction in the contact chamber gave a solid, sodium sulfide, which melts about 750° F. This is a difficult product to handle as it is extremely hard and plugs up the equipment. It sinks to the bottom of the liquid sodium allowing the sodium to function until a deposit is built up which covers the inlet from the still. The experiment ended abruptly at this point.

Since the gasoline was free of gum and sulfur, it required no further treatment, testing negative to the doctor test and non-corrosion.

These results were of sufficient interest to follow up. A semi-plant unit was designed and constructed whereby an attempt to work out a commercial plant was attempted.

Fuel from a pipe still was used as the heating medium for the sodium and to keep the contact chamber hot during the experiment. This contact chamber was built so that the sodium sulfide would drop into the bottom section and the excess sodium would gravitate into the heating chamber. A centrifugal pump was used to force the sodium into the contact chamber, where it was broken up into a fine spray and in this form was sprayed into the gasoline vapors.

Numerous test runs were made but it was found that the results were the same. The gasoline came out,



Bubble Tower Showing Internal Stripping Sections

carrying a finely divided mist of sodium that could not be removed by settling or filtering. This sodium mist drops out on standing over a long period of time, but as is common to all storage tanks, a small amount of water produces a violent explosion.

The constant danger of an explosion is present during the operation, as there is a small amount of water formed during dry distillation of petroleum, and this water causes a violent action on the part of the sodium.

Sodium is the one perfect substance that has been found that will entirely remove all of the sulfur compounds in gasoline; but a commercial application has not found its way into commercial channels as yet.

Octane Requirements Forcing Cracking Expansion

GEORGE REID

"WAY back in the old days" of 1923, Refiner and Natural Gasoline Manufacturer published a series of editorials, economic analyses and descriptions of the cracking processes then available, and stressed the fact that the future of the refining industry was closely interwoven with the future progress made in the development of the cracking art. It is believed that the same reasoning applies today—and the refiner not possessed of cracking facilities will find it increasingly difficult to compete with his more efficient neighbors and to market his relatively low anti-knock rating motor fuels. And the trend is still toward higher octane rating.

STRAIGHT RUN gasoline has definitely lost its market dominance. Unless some radical change is brought about in internal combustion engine design which will permit of the utilization of low anti-knock value gasolines, cracked gasoline has permanently displaced the natural crude gasoline, and in displacing it, has made the natural product virtually a drug on the market.

The present Ethyl Standard of 78 Octane number, effective March 1, contributes to further decrease in demand for straight run gasolines, and unless more and more of it is "reformed" stocks must be affected upwardly. It is apparent that the refinery without cracking facilities had better start "doing something about it."

A study of the crude oil charging capacity of most of the large refineries of this country indicates that the production of straight run gasoline is too large and that cracking facilities at most plants are not equal to the task of producing sufficient cracked gasoline to provide blending material in large enough quantities to produce enough high octane number motor fuel. The motorists of this country are not reversing practices of a year ago and purchasing low octane rating gasoline as offered in the third grade. They are buying medium or high octane rating fuels in accord with the demands or performance of their individual automobiles.

Such plants as mentioned above, and the larger number of American refineries fall into this classification, must enlarge their cracking departments either through utilization of naphtha reforming units or additional gas oil or fuel oil charging liquid or vapor phase cracking units, or the units taking crude direct and performing the functions of cracking and skimming through the use of one furnace.

LESS CRUDE—MORE GASOLINE

The unusual situation exists this year wherein the refining industry will of necessity spend many millions of dollars for additional refining facilities (cracking units, recovery and stabilization plants) and will run less crude to still than the previous year, yet produce more gasoline. The cracking units will contribute the higher octane rating fuels demanded this year (and next) securing a high percentage recovery from the crude run and meet an increase in motor fuel demand estimated at eight-tenths of one per cent above the demand figure for 1931.

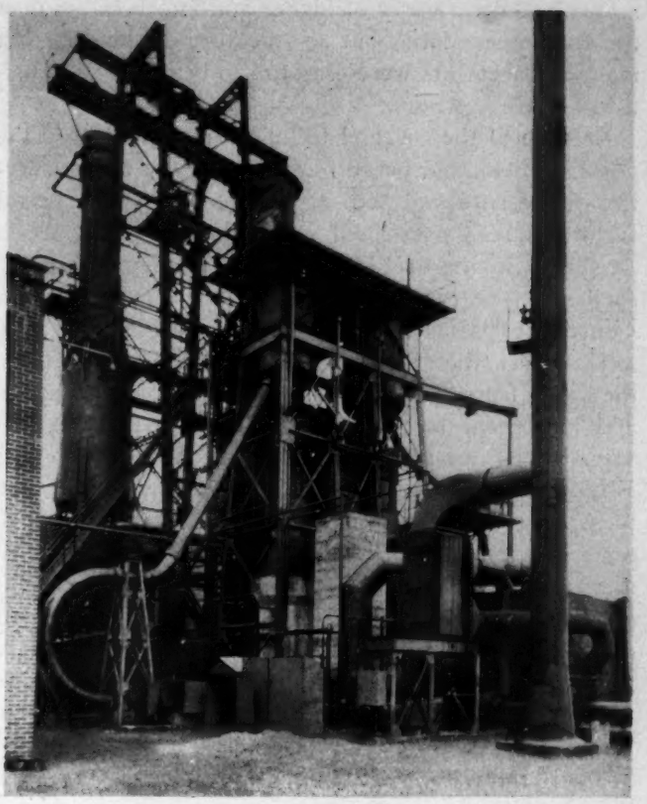
According to the estimates published in February (Ref. & N. G. M., Vol. 11, No. 2, Feb. 1932, Page 89A-91A.) as to crude runs, gasoline yield and demand, H. J. Struth, Staff Economist, states that the refining industry in 1932 will duplicate its history of 1931, running less crude but producing more gasoline. Crude runs last year were 893,622,000 barrels as against 927,447,000 barrels in 1930, and 1932 will see crude runs estimated at 850,000,000 barrels, or a decrease of 40,000,000 barrels for the year. Gasoline yield is estimated at 45.5 per cent. Domestic gasoline demand will probably amount to 406,175,000 barrels as compared with 402,000,000 barrels in 1931.

THIRD GRADE NO HELP

Sales of third grade gasoline (most of which is straight run) are not sufficiently large to absorb the surplus of natural motor fuel and the new Ethyl Standard of 78 Octane number for premium fuels has assisted in bringing about the condition wherein additional cracked gasoline must be provided to assist in the absorption of the straight run and to reduce the use of "lead" at least within the range allowed. The Ethyl Standard was raised from 74 to 78 Octane number because competitive conditions within the industry had brought about a condition where much of the gasoline being marketed (some not ethylized) was above the older standard.

In May of 1931 and in several later issues of this magazine it was pointed out that the year 1932 would

GROWING appreciation on the part of the American motorist of the performance of modern high compression motors and competitive conditions in the marketing of petroleum products have brought about a condition in the refining industry where the refinery not equipped with cracking facilities "must do something about it." Straight run gasoline has permanently lost its once dominant position in the market and the trend in manufacturing and demand points definitely to further increases in production of cracked motor fuels.



see a marked revival of construction in the refining industry in order to provide improvement in the anti-knock qualities of the industry's motor fuel. A study of the department of Plant Activities, Month in Review Section, of this magazine for January, February, March and April, will confirm the accuracy of those earlier opinions or predictions.

When the announcement came later last fall to the effect that the Ethyl standard would be raised from 74 to 78 Octane, the refining industry found itself confronted with the task of erecting a large number of various types of cracking processes, and of doing it quickly. During the weeks of uncertainty as to whether Ethyl Gasoline Corporation would go through with its proposed plan of distributing its "Q" compound for use with a second grade of anti-knock motor fuel, or "Ethylized Regular" (proposed early in November, 1931, to become effective March 1, 1932) it was the view of many refiners that under such conditions the industry might avoid a vigorous campaign of new cracking unit erection, or at least defer it for possibly a year or two.

However, it is reported that refiners in this country brought about the later retraction of the offer and for the time being "Q" compound lies dormant. Ethyl standard is raised to 78 Octane and large appropriations have been made and are being made for the construction of cracking facilities. The automotive industry is increasing its compression ratios and wishes to go further in this direction, as the American motorist is partial to high compression motor because of its improved performance.

MOTOR FUEL STANDARDS RAISED

Not only have the premium grades of gasoline been improved for the satisfaction of motorists possessing modern engines, but competitive conditions within the industry have brought about a marked improvement in the regular grades of fuels offered. In addition there is at present a tendency to improve the third grade motor fuel and to offer it as a really good motor fuel. To be sure, several companies are apparently still instructing service station men to depreciate the value of the third grade and its sale is not pushed but is rather retarded through these efforts. Such an attitude has incurred much criticism from both public and oil company officials. On the other hand a few companies have reversed their tactics and are now improving the quality of this grade of fuel, offering it as a quality product, and as this quality improves there is opened another avenue for the more extensive application of the cracking process.

REPLACEMENTS

The present campaign of cracking unit erection by American refineries was necessary not only because of increased public demand for better motor fuels (aided by competitive conditions within the industry) and the increase in Ethyl standard (brought about partly because refiners were marketing premium fuels in various

sections of the country of higher anti-knock rating than the former standard) but also because of the fact that many replacements were essential to efficient manufacture or safe operation.

Because of the constant technical improvement in the cracking field, and because of the severity of the service, obsolesence and "old age" become very important factors in both liquid and vapor phase cracking work. At the beginning of 1931, for example, there were 825 shell still type cracking units reported in this country, (Bureau of Mines, Survey of Cracking Plants, Jan. 1931, Information Circular No. 6509). All of these, in the light of present progress, are obsolete, uneconomical and inefficient in their operations, and, perhaps, unsafe. Their total capacity reported at that time was 171,921 barrels. It is estimated that about one-third of them have been dismantled this year, or converted to other service. It is further estimated that the present capacity of this older type of cracking equipment is around 115,000 barrels. Basing newly constructed units of modern type at an average capacity of 3000 barrels per unit, the replacing of this type of cracking equipment will involve the erection of 35 to 40 units. Approximately half of this replaceable capacity is located at the refineries of the 20 major companies operating in the United States.

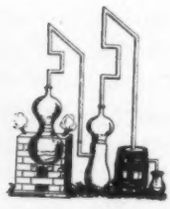
In addition, many of the pipe still type cracking units installed and operating at the time of the first survey of the Bureau of Mines, 1925, are now obsolete and unsafe for further operation. Inasmuch as such abandonment replacement is essential and under way, the Bureau report for 1932 (not yet released) will in all likelihood show still further decrease in total number of cracking units, while also showing a further increase in total operable capacity. This has been the trend during the past seven years since the high point of 2559 units in service was reached in 1926. The 1931 survey reported 1868 units, and as stated above, 825 of these were of the old shell still type, which are rapidly being abandoned.

It is interesting to note in this connection that around 650 of the remaining 1150 tube still cracking units are at present licensed by two concerns, Gasoline Products Company, Inc. (Cross, de Florez, Holmes-Manley, Tube and Tank and combinations of various types) and Universal Oil Products Company, (Dubbs cracking process). Thus, between 55 and 60 per cent of the modern type units operating are of the types mentioned.

In their search for better efficiency of operation refining companies are studying the newer combination type cracking units which take crude direct to the unit, skim it, crack the heavier distillates, reform the heavier naphthas, all in one furnace. The largest unit of this type to be designed is being erected by Standard Oil Company (Indiana) with a capacity of 20,000 barrels daily.

With the aid of technical development and the application of the newer designs and general progress in the art of cracking, the refining industry is in position to supply the growing demand for fuels of higher Octane rating and will no doubt supply this demand at lower operating costs, securing increased yields from the crude.

While there is a possibility of some radical change being effected in the automotive industry, as is discussed elsewhere in this issue with regard to "solid injection" of motor fuels into the cylinders of the internal combustion engine, which may effect gasoline specifications even to the extent of changing views toward anti-knock ratings, such developments are as yet but experimental and the effects of a possible utilization of such devices by the automotive industry cannot yet be appraised.



Solid Injection—A Look Into The Future of Motor Fuels

EARL PETTY*
Chemical Engineer

THERE has always been quite a "lag" or "gulf" between the engine and automobile manufacturers and the refiner. This is brought about largely because of the distinct industry divisions and subdivisions. The automobile industry is divided into one class of manufacturers making and turning out the final product. Serving this industry is a subdivision known as the accessory manufacturers. This subdivision is responsible for the development of the minor accessories which are first developed entirely separate from the engine or automobile manufacturer. For example, no automobile or engine manufacturer manufactures his own carburetor. There are half a dozen specialized manufacturers competing for this accessory. With this set up and arrangement it is possible for a gap or lag of a year or more to develop along the lines of certain improvements and trends before the innovation actually reached commercialization. Until the device reaches the automobile manufacturer it might or might not come to the attention of the refiner. It is the general rule that the automotive industry builds and develops a device or improvement which has certain requirements and then they ask the refiner to make a product that will perform satisfactorily.

This condition has been lamented and discussed in various connections and this article deals with a development that might be "sprung" on our industry within the next year and the following discussion is intended to point out some of the developments which will be effected.

Today our motor fuel "gasoline" is surrounded by a number of very special specifications and physical characteristics which are not necessarily fundamental so far as thermodynamic requirements are concerned but are essential in order to operate through the conventional device known as a carburetor. Through a combination of circumstances the automotive engine and the refining industry inherited this device and it has meant no end of trouble in trying to make a product that, when metered into the engine through it, would give the satisfactory power result.

We have gone along so long producing and developing a fuel for the conventional carburetor that we do not realize how closely our finished product has been confined just to meet the fundamental requirements of this device. Our entire light ends operation and handling methods reflect the requirements of the carburetor.

If we stop to analyze the device and its principle of operation we find that it determines the major characteristics of our fuel. After the fuel is delivered to the cylinder there is an entirely different set of requirements but the problem is purely thermodynamic and the variety of fuels are much broader, or in other words, the requirements are less exacting.

Detailed analysis of the carburetor reveals the following points:

First. It is the point of control of the air necessary for combustion.

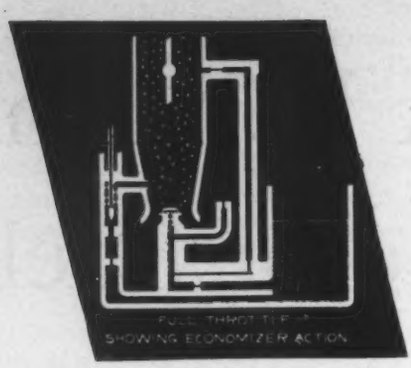
Second. It is the apparatus for metering the fuel.

Third. The items one and two are proportioned by this device to give the proper air-fuel ratio.

Fourth. The mixture of the fuel and air is accomplished in this device and started on its path of delivery to the motor through the manifold system. In the manifold is located the conventional hot spot which serves to bring about a more perfect and homogenous mixture of fuel and air. The mixture is purely a product of physical results of entrainment and air distillation. The bond established by air distillation is fixed by the additional heat of the hot spot and the stored temperature of the cylinder but it is offset by the effect of surface condensation, and by the initial compression, both of which tend to cause condensation of heavier ends of the fuel. Therefore the fuel has to be made with characteristics that will give a perfect vapor under the above conditions.

Fifth. By constriction and restriction of the air passage, due to the suction of air capacity of the piston on its downward stroke, a condition of reduced pressure is brought about and at this point, the liquid fuel is exposed or subjected to the reduced pressure over a device known as spray bar nozzle or jet. This condition, combined with the high velocity of the air through the throat of the carburetor, causes the fuel to be picked up

*Bethlehem Steel Company.



Stromberg carburetor, showing construction of air path and fuel pick-up into air stream. This section is from a carburetor of the type most commonly used on aircraft engines.

by the air stream with the result that it is mechanically atomized. (See sketch).)

Sixth. At the same time certain processes and effects of air distillation are effected so that by a combination of mechanical and physical actions the fuel is partly vaporized by air distillation and partial pressure effect and partly carried by entrainment as a gas or vapor.

From the above analysis it is very evident that this device has established the following characteristics of our "gasoline."

Initial point, to prevent vapor-locking;

Five per cent to 35 per cent point for starting;

Type of boiling curve to give best results for air-distillation;

End point, to insure that all of the fuel can be carried either as a vapor or with a small per cent as mist by entrainment.

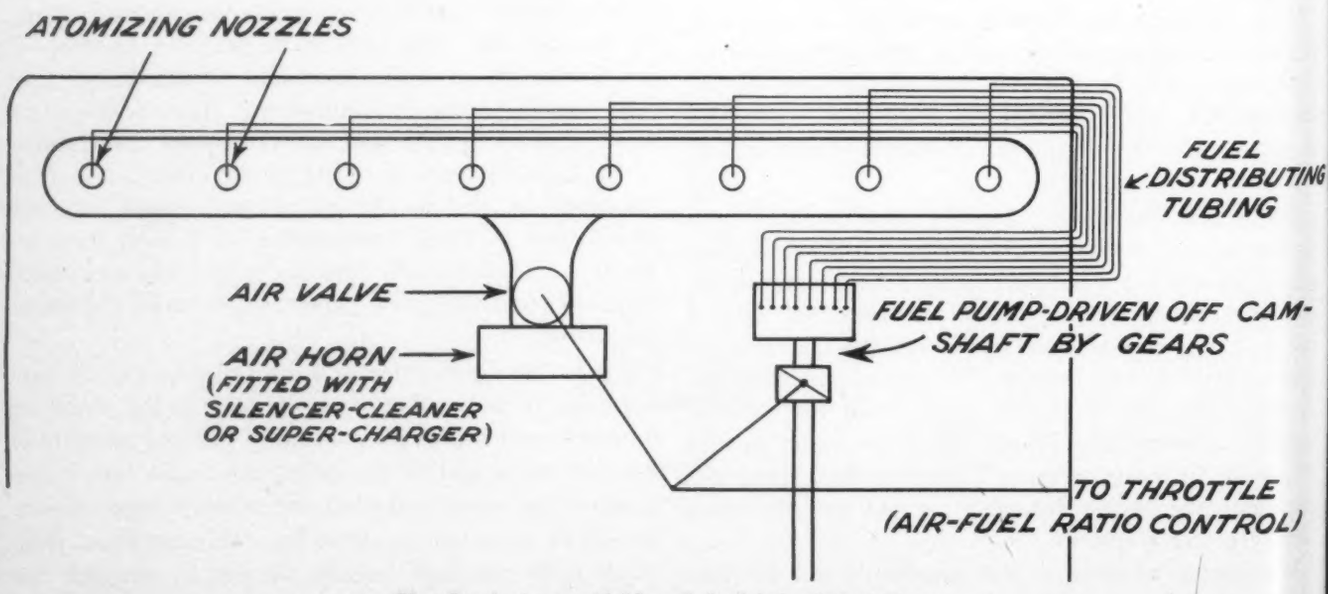
The characteristic of detonation is entirely independent of the conventional carburetor device and is primarily a factor of the actual combustion and power delivery. Gum is a chemical problem, also independent of the carburetor. Sulphur also is a chemical problem and vital only so far as corrosion and metallurgic consideration are concerned.

Those familiar with the "Otto-cycle internal-combustion" engine realize that an engine is no better as a power generator than it is as an air pump because the amount of air that can be taken in directly determines its maximum power output, since no more fuel can be taken in than there is air (oxygen) available with which to burn the fuel.

In the analysis of the carburetor we found two distinct interferences to the volumetric capacity of the engine, viz.: pressure drop due to constrictions, and actual mechanical load of carrying the fuel. The conditions about the jet necessary to pick up the fuel bring about a pressure drop which means that at the time the cylinder is taking in air the entire manifold system back to the jet is under vacuum or reduced pressure. This brings about a rarified condition which means that the cylinder will get less oxygen than it would if the air were under atmospheric pressure. At the same time, the air that is being taken in serves as an endless belt conveyor with the actual weight of the fuel as a burden. The result of these two factors is that the air capacity of the cylinder is materially reduced.

Two years ago accessory manufacturers found that they could substitute a fuel pump for the vacuum tank with an increased power result. This was due to the fact that the fuel system using a vacuum tank was putting a further load on a vital requirement of the engine for air. In other words, just at the time the most air was required for maximum power, a greater quantity of fuel was required and this had to be lifted at a direct reduction in the available air. The mechanical fuel pump was substituted and the engines were given greater pick-up and greater power.

The result was that at the automobile show this year not a single vacuum tank was to be seen on automobiles.


ATOMIZING NOZZLES
FUEL DISTRIBUTING TUBING
AIR VALVE
AIR HORN (FITTED WITH SILENCER-CLEANER OR SUPER-CHARGER)
FUEL PUMP-DRIVEN OFF CAM-SHAFT BY GEARS
TO THROTTLE (AIR-FUEL RATIO CONTROL)

Sketch of air manifold and fuel injection system.

This little fuel pump eliminated quite a few difficulties, among which was considerable relief of the vapor lock problem. However, there is still trouble with this feature in the carburetor device itself.

In connection with Diesel-cycle engine development we have been depending on an entirely different system of getting the fuel into the engines, namely, mechanical injection.

Theoretically the Diesel-cycle is much more efficient than the Otto-cycle. However, the Diesel principle involves certain handicaps which have limited its development and adaptation for automotive uses. On the other hand, the Otto-cycle has certain advantages due to light weight per horsepower that has kept it in the automotive field as the most practical and popular type of engine.

For some time the idea of using the mechanical system of injection has been receiving attention and development. At the same time the carburetor was receiving so many improvements that due to its conventional use it was able to stay in the foreground.

From an engineering standpoint a device or apparatus may reach a "perfected" stage but it is never "perfect." The carburetor has reached that "perfected" stage and at this point its inherent handicaps become conspicuously large.

With carburetors of today and the marvelous response from motors in combination with a "perfected" fuel, it is found that the combination cannot be radically improved along the present lines. We find that we have reached the limit of power output per pound of fuel and steel—all for the lack of a little more oxygen or air.

The first thought would naturally be to improve the air pumping efficiency of the motor. Natural reasoning would suggest that we eliminate the obstructions in the air path. This brings us to a real problem—elimination of pressure drop and the fuel load.

Here is where one line of development turns to its competitor or contemporary and borrows an idea. Why not the Otto-cycle engine borrow the solid injection system from the Diesel-cycle?. This is exactly what has been done. The new combination is something along the following lines:

First. A mechanical pump system with a distribution system is developed which is similar in principle of operation to the electrical distributor. It is driven in the same way and the fuel stroke is timed with the air intake stroke.

Second. The manifold system is nothing but an air system and may be under pressure of the atmosphere or artificially super-charged.

Third. A throttle system controls the air-fuel-ratio by simultaneously adjusting the amount of air and the stroke of the pump delivering the fuel.

The system above outlined accomplishes the following results:

First. The fuel is metered mechanically and positive-

New Type Hornet Engine

(*From Aero Digest, January,* 1932)

A NEW type Hornet aeronautical engine utilizing the principal of *atomization and injection of gasoline direct to the cylinder chamber has successfully completed its dynamometer* and flight tests and has been installed in a Boeing 40-B-4 mail plane on the Boeing division of the United Air Lines for the purpose of determining its desirability under service conditions. The Pratt & Whitney Aircraft Company of East Hartford, Connecticut, a division of the United Aircraft & Transport Corporation, after more than a year's experimentation with this new method of fuel distribution, has been successful in perfecting the mechanisms which permit the elimination of the fuel distribution problems encountered with the use of carburetor, air scoop and preheater.

The Hornet equipped with this new device develops in excess of 525 horsepower and with the exception of the fuel distributing system is essentially the same as the Series A-2 Hornet. By the direct injection of gasoline as provided by this new departure in fuel distribution, the hazards of cold weather operation are completely overcome. Perfect operation is assured regardless of the air temperature. Cold starting is greatly facilitated and the difficulty previously encountered with ice formation in the carburetor during winter operation is eliminated.

The fuel injection Hornet is an important step toward the utilization of less inflammable fuels such as the hydrogenated or safety fuel produced after exhaustive experiments by the technicians of the Standard Oil Company of New Jersey, according to A. V. D. Willgoos, Chief Engineer of the Pratt & Whitney Aricraft Company. It is believed that future developments of this model will use such fuels with the same efficiency as gasoline. It is produced by the hydrogenation process with particular attention to high flash qualities and has an octane number of 82.6 without the addition of any knock suppressor. Experiments have indicated that fuels produced by the hydrogenation process have inherent anti-knock value—a characteristic of great importance to aircraft engines. The Temperature at which the fuel will ignite is 107 degrees F. as compared with the flash point of ordinary gas which is anywhere from 28 degrees F. to 46 degrees F. The non-inflammable characteristic of the fuel at low temperatures will insure against possible fire in crash.

The engine has successfully passed its rigid 50-hour block test and has proved itself efficient in every flight test.

The engine will not be offered to the trade for general use at this time.

▼

ly and is distributed in exact quantities directly to a section of the manifold adjoining the intake valve of the cylinder for which it is intended, thus the distribution problems of the conventional-carburetor-manifold system is completely solved. (With the conventional carburetor system multiple jets and bowls and even complete carburetor unit duplicates have been used on multiple cylinder engines in order to improve the distribution conditions.)

Second. The fuel is mechanically atomized directly into the air stream. The air can be drawn over the conventional hot spot and heated so that it will make a more permanent and homogenous mixture when it strikes the mechanically atomized oil. This mixture is taken directly into the cylinder where it comes immediately under the conditions of stored heat and then the heat of compression, with a result that a perfectly mixed and explosive mixture is produced.

Third. The peak power output is increased from 10 to 15 per cent.

Fourth. The engine is more responsive since the fuel is handled mechanically and positively.

Fifth. Starting is improved as the fuel is mechanically atomized and vaporized at a point immediately adjoining the intake valve.

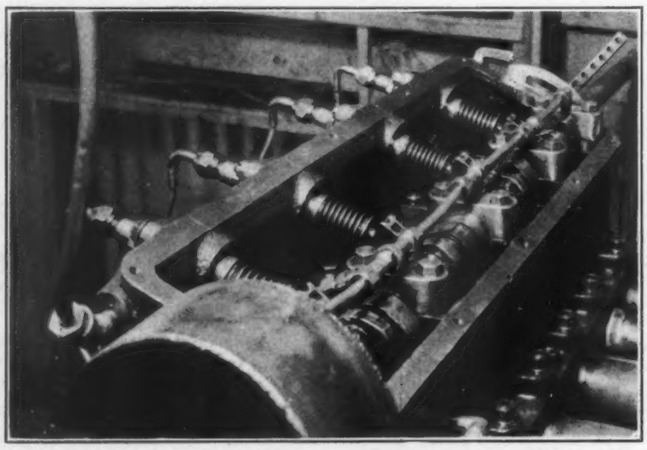
Commercial tests (using this system of fuel handling and injection) has been under way for over a year on trucks, automobiles, and aeroplane motors. In these tests a number of types and varieties of fuels have been tried.

Here is where the really striking and serious results and possibilities have been found and these will be of vital interest to refiners. In the first place a number of requirements imposed by the conventional carburetor have been completely eliminated.

It has been found that fuels of entirely different boiling characteristics can be burned with surprising results. For example a special safety fuel for aeroplanes of 323 I.B.P. and 397° F. end point, gave perfect performance as compared with ordinary gasoline. Special heating of the air was necessary for starting with this fuel, but once in operation it gave perfect performance. Other tests have been made on truck and bus motors, using blends of gasoline and gas oil, and or furnace oil, and or kerosene. These mixtures had only enough gasoline to make starting possible but with end point of from 550 to 660° F. These fuels also gave satisfactory performance. Other tests have been made with large mixtures and high percentages of the lighter compounds which usually bring about difficulties of vapor locking. This trouble was eliminated because the liquid system is handled entirely by pumps and is at all times under pressure of from five to 250 pounds per square inch.

It will be readily seen that the various demonstrations above begin to upset a number of specifications, requirements, and characters about which the entire refining industry has been developed, viz.: control of boiling range, fractionation, per cent of fraction for motor fuel, and stabilization. What might a device of this kind mean to the refining industry if it would suddenly appear as standard equipment on all automobile and airplane engines? There is enough of its shadow already visible and coming from research and development laboratories of the automobile accessory industry to warrant careful consideration and study.

In a later article some developments for burning heavier oils such as kerosene, furnace distillate and gas oil will be discussed and also developments for improvement and control of anti-knock characteristics by novel pre-combustion process and apparatus. These developments, together with the above discussion, have considerable bearing upon another fuel characteristic about which the refining industry has gone to considerable trouble, viz.: detonation.



(Courtesy The Guiberson Diesel Engine Company, Dallas Texas.)

View of Fuel Pumps and Control on Guiberson Diesel Truck Engine

Increasing Octane Values in Gasoline Through Design and Operation of Reforming Units

Paper read before Western Petroleum Refiners Association, Excelsior Springs, Mo., April, 1932

W. A. GOLTRAP*

JUST as the increasing number of automobiles created the demand for enormously increased supplies of gasoline and furnished the stimulus for the development of the cracking process, in like manner at a more recent date, the increased quality of the gasoline necessary to meet the more rigid requirements of the improved engines, lead to further research and development work to provide a supply of this motor fuel. One of the outstanding results of this research and development work has been to increase the quality of the motor fuel with respect to its anti-knock value.

Automobile engineers, faced with keen competition, were and are constantly seeking greater efficiency and better performance in their engines. From research work carried on, it was definitely established that by increasing the compression ratio of the engines, greater power, faster pick-up, better fuel economy and an improved all-around performance would be obtained.

In the operation of high compression engines a fuel is required which possesses different characteristics from the motor fuels that have been previously used in the lower compression engines. A motor fuel that does not "knock" or "ping" gives the smoothest and most efficient operation and this fuel has come to be known as anti-knock gasoline.

Petroleum technologists in their search for motor fuels to give the results desired, found that cracked gasoline when used separately in the internal combustion engine, gives superior and more satisfactory results than the average straight-run gasoline. This quality for better performance soon created a situation which called for a greater amount of unblended cracked gasoline, making it more and more difficult to dispose of straight-run or blended gasoline. This situation has become increasingly worse until today the stocks of straight-run gasoline are increasing rapidly and out of proportion to the cracked motor fuels.

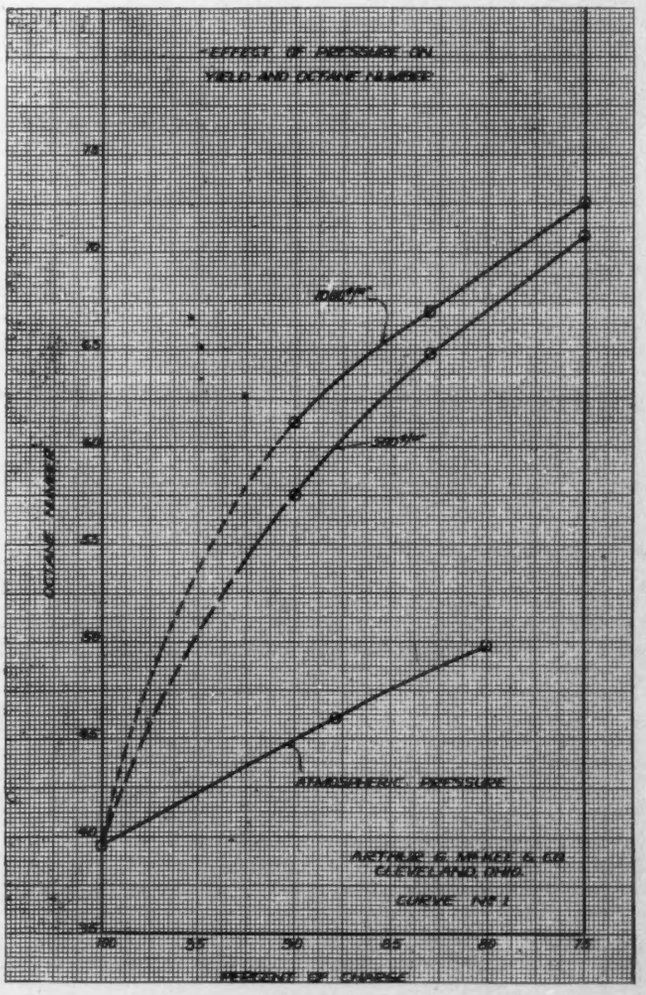
The research and development work as previously referred to, developed that straight-run gasolines and heavy naphthas could be cracked and in this operation a good recovery of gasoline having high anti-knock quality could be obtained.

In the development of the discussion on design and operation of reforming units, flow diagrams have been drawn up showing various types of units for cracking straight-run gasoline and naphtha.

(1)—Flow Diagram No. 1, shows one type of unit recommended for this operation.

(2)—Flow Diagram No. 2, is a unit similar to No. 1, but without a reaction chamber.

(3)—Flow Diagram No. 3 is of a unit in which the reaction chamber has been eliminated



*Arthur G. McKee & Co., 2422 Euclid Avenue, Cleveland, Ohio.

and in which the flash drum has been incorporated in the tower. A high temperature and pressure heat exchanger has been incorporated through which hot material from the heater passes and exchanges heat with the cold charge.

The flow diagrams show the flow of material through the various units together with the main items of equipment.

In the unit shown in Flow Diagram No. 1, gasoline or naphtha is pumped by a high pressure pump through a vapor heat exchanger located in the vapor line between the flash drum and the bubble tower. Hot recycle stock is picked up from the bottom of the bubble tower with a second high pressure pump and discharged into the fresh feed charging line before entering the heat exchanger. From the heat exchanger, the combined charge passes to the heater where it is raised to the required cracking temperature. From the heater, the material enters the top of a vertical insulated reaction chamber held under full operating pressure. Here the material is allowed to remain for sufficient time to complete the cracking reaction.

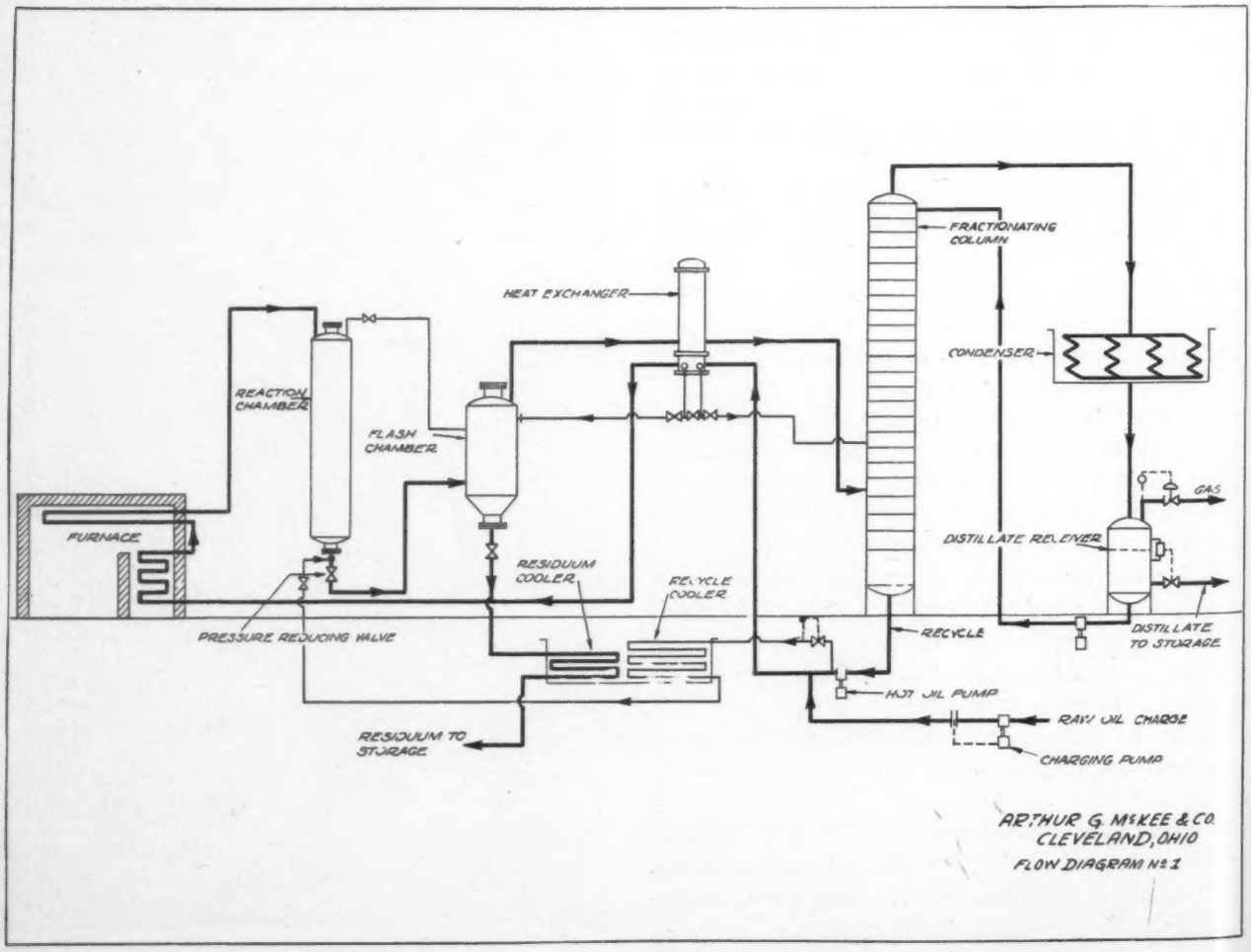
From the reaction chamber, the material is discharged to the flash chamber through a pressure reducing valve.

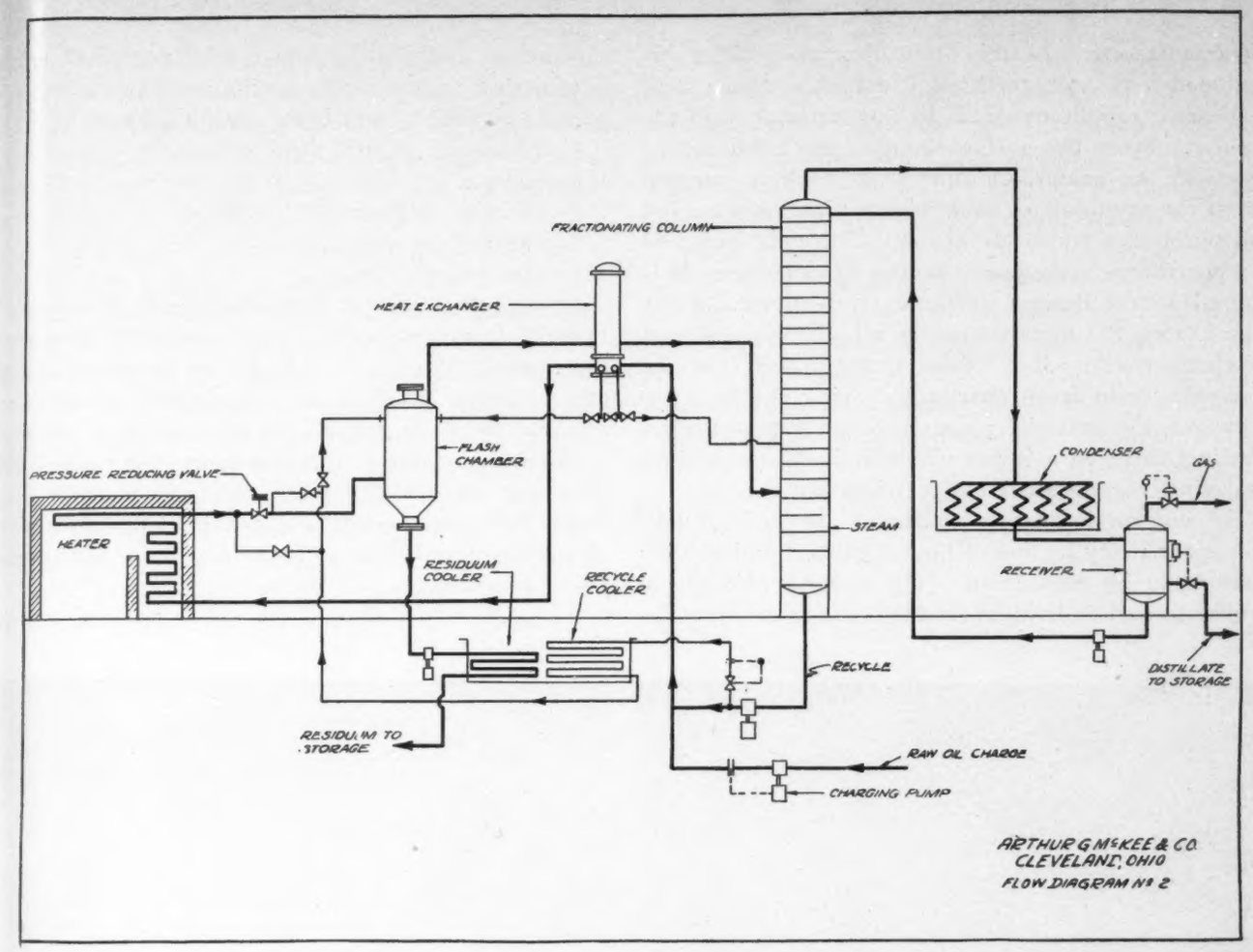
In the flash chamber, the fixed gas, gasoline vapor, and recycle stock vapors pass up through refluxed bubble trays, where any entrained tar is separated, passes to the bottom section, and is continuously withdrawn as liquid through a cooler to storage. The scrubbed gas and vapors leave the top of the flash drum through a high pressure heat exchanger, counter-current to the incoming charge stock, and go to the fractionating tower. The fixed gas and gasoline vapors pass up the column through rectifying trays, counter-current to liquid reflux, which removes any high boiling recycle stock and leave the top of the column through a condenser and cooler to the distillate receiver. Here the fixed gas and distillate are separated, the gas going to the gas recovery system while the distillate goes to the stabilizer unit. Hot liquid recycle stock collects in the bottom of the fractionating column and from there is recharged through the system.

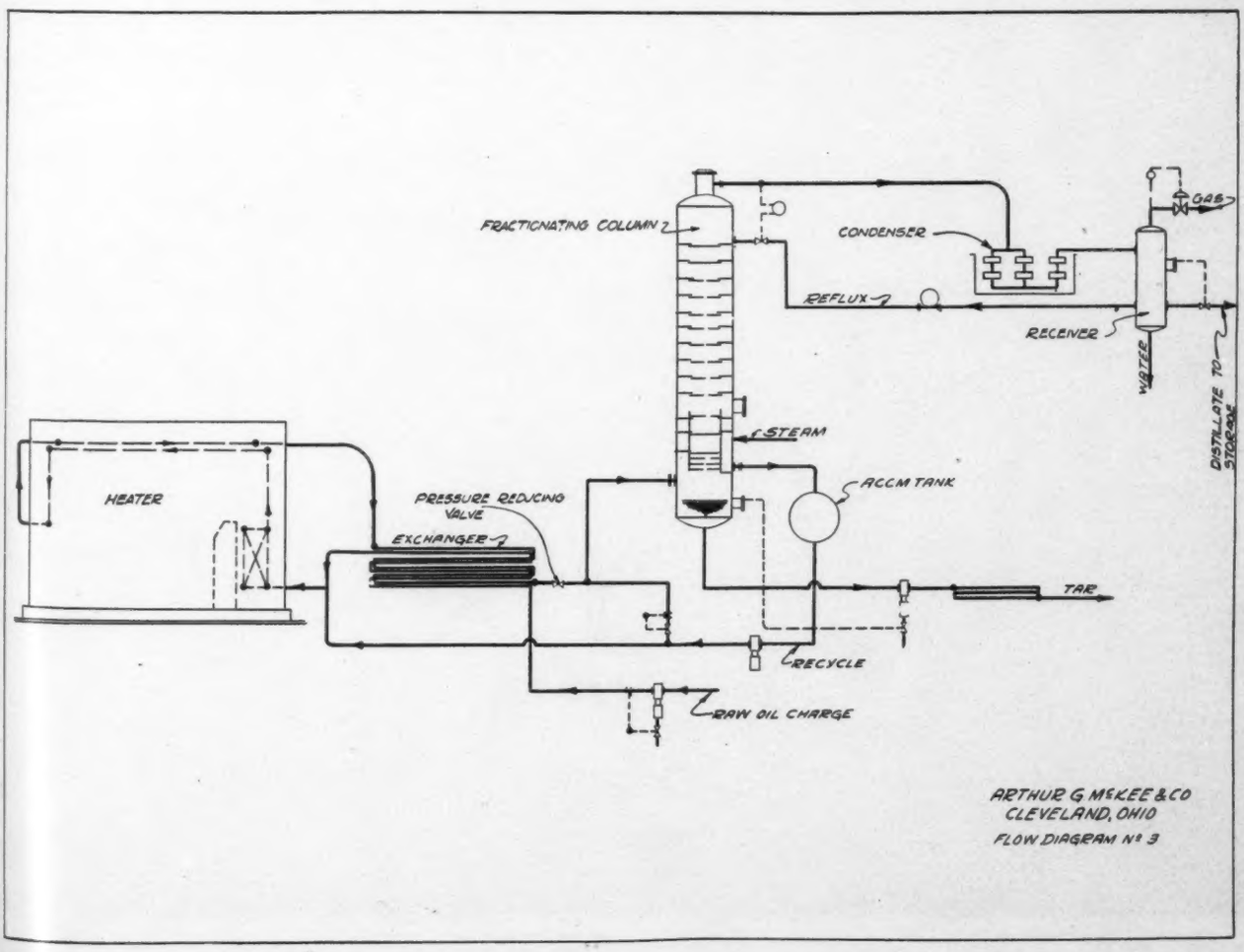
This very briefly describes the flow of material through the system.

Flow Diagram No. 2 shows another cracking unit without the reaction chamber. Eliminating the reaction chamber, the flow of material and main items of equipment are the same as for the unit shown in Flow Diagram No. 1.

The unit shown in Flow Diagram No. 3 consists of a heater, high pressure heat exchanger and bubble tower, together with the necessary lines, pumps, in-




FRACTIONATING COLUMN
HEAT EXCHANGER
FLASH CHAMBER
PRESSURE REDUCING VALVE
HEATER
RESIDUUM COOLER
RECYCLE COOLER
CONDENSER
GAS
STEAM
RECEIVER
RECYCLE
DISTILLATE TO STORAGE
RESIDUUM TO STORAGE
RAW OIL CHARGE
CHARGING PUMP
ARTHUR G McKEE & CO.
CLEVELAND, OHIO
FLOW DIAGRAM No 2


FRACTIONATING COLUMN
CONDENSER
GAS
REFLUX
RECEIVER
WATER
DISTILLATE TO STORAGE
STEAM
ACCM TANK
HEATER
PRESSURE REDUCING VALVE
EXCHANGER
TAR
RECYCLE
RAW OIL CHARGE
ARTHUR G McKEE & CO
CLEVELAND, OHIO
FLOW DIAGRAM No 3

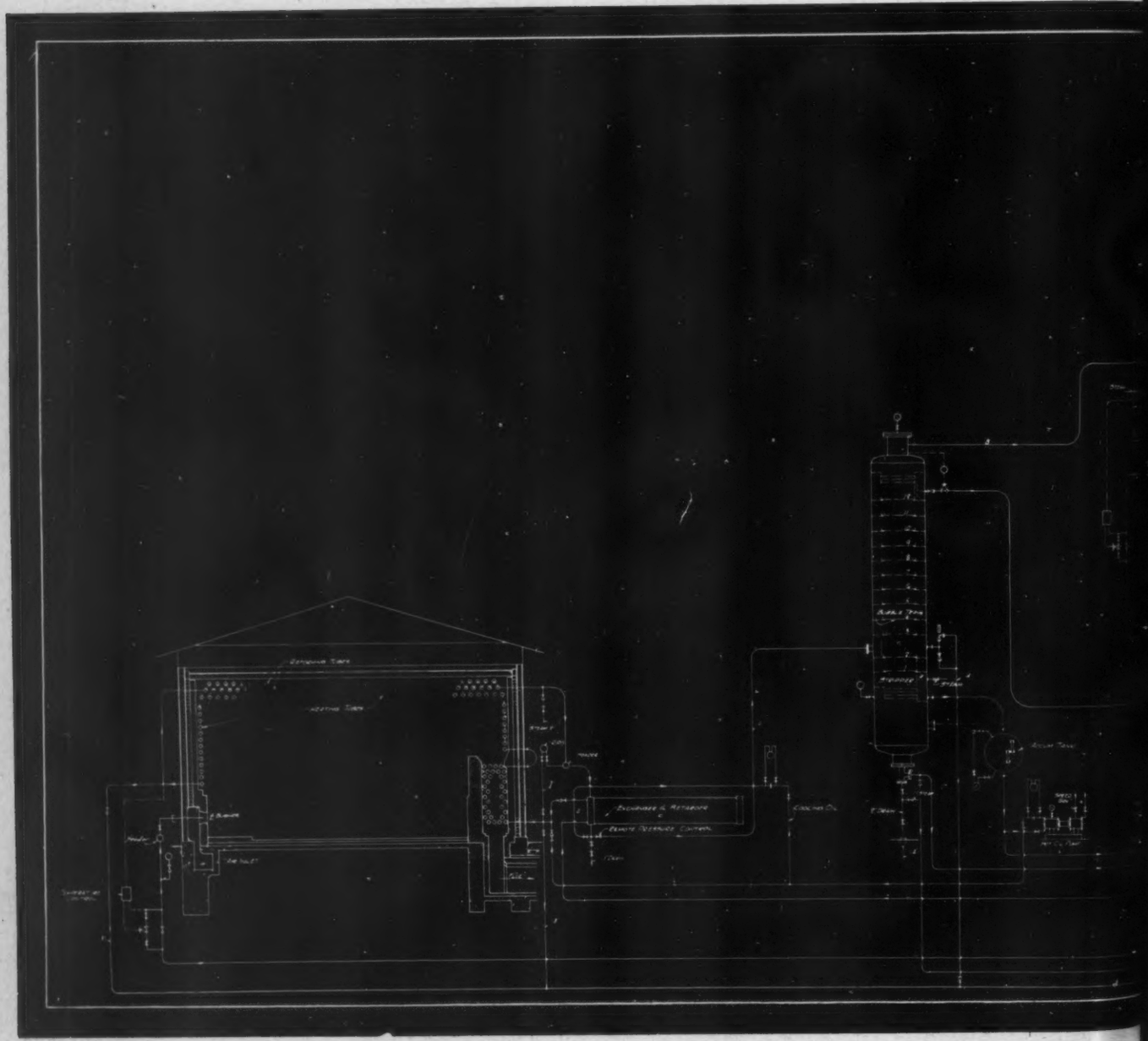
struments, etc. In this unit, the fresh charge is pumped from storage through a high pressure heat exchanger, counter-current to the material from the heater. From the heat exchanger, the fresh charge goes to the heater. Hot recycle stock is pumped from the accumulator tank with a high pressure hot oil pump directly to the heater. The combined feed passes through the tubes in the heater where it is raised to the desired cracking temperature. From the heater, the material enters a high pressure heat exchanger where it is cooled under pressure by the incoming cold fresh charge. Leaving the heat exchanger, the material passes through a pressure reducing valve to a tower where it is separated into gasoline, recycle stock and cracked tar.

In considering or evaluating a reforming unit, there are many factors of both a general and specific nature to be considered. The specific factors peculiar to each individual case will not be discussed in this paper; but they should not be neglected when considering an installation. Some of the more important general factors to be considered are:

1—Flexibility.
2—Yields.
3—Quality of Products Produced.
4—Initial Investment.
5—Operating Costs.

A reforming unit is a cracking unit so designed that the optimum conditions of time and temperature for cracking gasoline or naphtha can be produced and any charging stock from straight-run gasoline or naphtha to heavy gas oil, can be cracked in the unit by maintaining the proper conditions for each stock. Cracking units of the latest design, constructed to crack kerosene or gas oil, are actually reforming straight-run gasoline and naphtha into high anti-knock gasoline.

The choice of unit will depend upon local condi-



tions, charging stock and flexibility desired. While Unit No. 1 costs more than either Units No. 2 or No. 3, it is suitable for a wide range of charging stock. The operating costs of all three types are about the same and will average about 25 cents per barrel of fresh feed.

As measured by previous standards, reforming of straight-run gasoline or naphtha is not a profitable operation. However, with the increased specification in quality of the gasoline, from an anti-knock value now demanded, the refiner in many instances is or will be forced to crack straight-run gasoline and naphtha in order that the total yield of his gasoline from the crude processed, can be marketed at the premium price for anti-knock fuel.

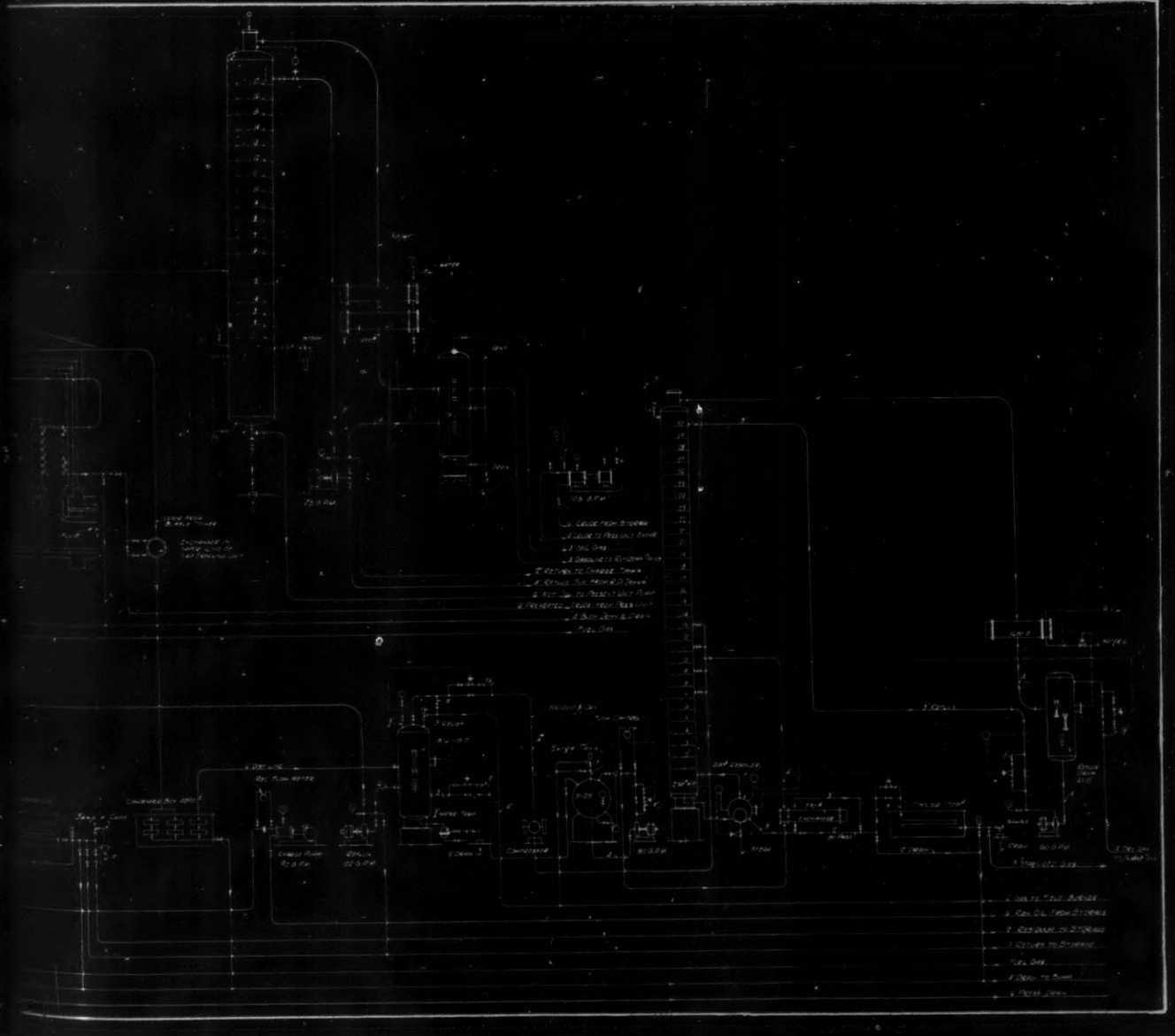
By reforming, the refiner will be able to dispose of all his straight-run gasoline in face of the continuous increase in octane number requirements for gasolines. The reforming operation in most instances, is the only possible way of bringing the quality of straight-run gasoline and naphtha within the range of a commercial product. With the establishing of a 78 octane number for the premium grade gasoline a base fuel of 59-60 octane number is required for Ethylizing to produce this premium fuel.

YIELDS AND SPECIFICATIONS OF PRODUCTS

Some concrete and specific results obtained when reforming low quality gasoline is no doubt of interest. In the following table, results set forth were obtained from the commercial cracking of straight-run Pennsylvania gasoline and heavy naphtha:

Charge	Gasoline	Naphtha
Cracked Gasoline	83.7%	84.4%
Residue	5.4%	4.8%
Gas and Loss	10.9%	10.8%
Total	100.0%	100.0%
Gas, Cubic Feet Per Barrel of Charge	346	295

(*Continued on page 289*)



The Bleaching Earths—A Laboratory Study

P. G. NUTTING
U. S. Geological Survey, Washington, D. C.

THE petroleum refining industry is the largest consumer of bleaching earths, using in 1930, 97.1 *per cent of total reported production in this country, and is therefore actively interested in any studies relative its properties and utilization. The accompanying laboratory study of P. G. Nutting, presented here by permission of the director of the U. S. Geological Survey, adds to the literature on this subject. The article, previously published in the Analytical Edition, Industrial and Engineering Chemistry, Jan.* 15, 1932, *has to do with sources, properties, and water contents of earths.*

CERTAIN igneous rocks, such as granite, basalt, dunite, diabase, and many others, when exposed to weathering, gradually break down both physically and chemically, the ultimate solid residue of the more profound types of weathering being largely inactive clays and soils. The original rock was composed of silicates high in bases, whereas the end products are secondary silicates, low in the more soluble bases but high in the oxides of iron and aluminum, and in silica.

Midway on the decomposition curves are the products that are typical of the active bleaching or filtering earths. Some of our best fuller's earth deposits are probably only the accumulated wash of partly decomposed igneous rocks which for some reason has not gone to soil or to inactive clay—typically the white and refractory clays. In a thoroughly weathered and partly bleached condition, simple drying at 160° to 190° C. is sufficient to drive off adsorbed water, leaving the free valencies or open bonds essential to the bleaching or filtering action. When the leaching is less profound, acid treatment may greatly increase bleaching power.

Some igneous dikes in Arkansas (1) decomposed *in situ* show decomposition to bleaching earth, to inactive ceramic clays, and to bauxite in neighboring parts of the same dike. Where the original rock was composed largely of the highly basic and complex minerals augite, hornblende, biotite, and (or) nontronite, the weathering was to fuller's earth which was formerly mined and shipped. Where it was feldspar, it has decomposed to kaolin, and where it was nepheline it is becoming bauxite. Here in Washington are exposures of decomposed granite showing the three chief products just described within a few yards. Near Bull Run, Virginia, is a decomposed diabase having excellent bleaching properties after sifting and acid-leaching.

Only sedimentary deposits of bleaching clay are now being worked in this country, since these are abundant and the expense of screening is avoided. The chief sources are Georgia, Florida, southern Illinois, Texas, Colorado, Utah, Nevada, Arizona and southern California. Several plants mine and mill as much as 10,000 tons per month. There is no production from glaciated areas. The bleaching clays were apparently brought down in large quantities of fresh water which kept the clay particles at or near their isoelectric points. Thus, soluble bases were removed from their surfaces (and replaced by H and OH) but not completely from their interiors. Complete leaching of minerals low in iron, with long contact with fresh water, would result in kaolin. The western bleaching clays are less leached, and a few of them of the bentonite type require an acid leach to activate them.

PROPERTIES OF EARTH

Neither chemical composition nor molecular structure as determined by x-ray analysis is sufficient to decide whether a mineral will be an active bleaching agent, since bleaching depends primarily on the condition of the surface rather than directly on composition or internal structure. The filtering material may be a simple hydrous oxide, a silicate, a glassy slag, ordinary glass, or volcanic ash. Activation may be said to consist in opening up the bonds over the surface (pores included) and the activity depends upon the extent of activated surface or number of open bonds per unit mass. As the writer has shown, it is possible to produce iron oxide, aluminum oxide, and silicon dioxide (2) in forms so active as to crack paraffin, and to activate the surface of even sea sand and crushed quartz crystals (3). Among the commercial fuller's earths, activities sufficient to crack paraffin, gasoline, or even the highly purified laxative oils are the rule.

The bleaching or filtering action (decolorizing and de-

odorizing, chiefly) of the active earths on oils and other solutions varies greatly with the solution that is to be filtered and with the filtering material used. Hydrocarbons like petroleum, which contain no OH groups, require the assistance of heat to drive the OH from the filtering material. Either the earth is first heated to 180° C. (160° to 200° C.) and then used dry, or else it

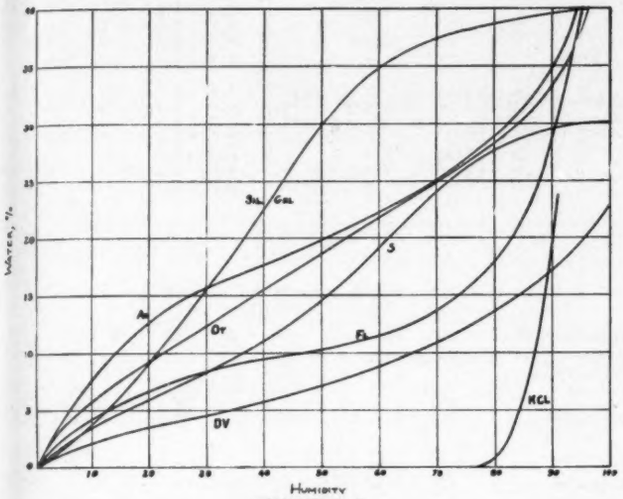


FIGURE 1
Water Content at Various Humidities at 26° C.

Fl, raw Floridin from Quincy, Fla.
DV, raw clay from Death Valley, Nev.
Ar, raw clay from Chambers, Ariz.
Ot, bentonite (Otaylite) from Otay, Calif.
Silica gel, powdered
KCl, powdered
S, powdered serpentine, acid treated, active

is heated to a similar temperature after oil and moist earth are mixed (the usual procedure). On the other hand such fluids as fish and vegetable oils, animal fats, and fruit juices, containing OH and with room for more, are filtered by moist and slightly basic filters, for their stronger ions can displace H and OH from the filter surfaces without the assistance of heat. Even a little base left in the filter is not objectionable. One neutral clay, filtering both hydrocarbons and animal fats about equally well, is composed of silicon dioxide, 69; iron or aluminum oxide, 16; calcium or magnesium oxide, 2; and potassium or sodium dioxide, 2.5 per cent, the rest chiefly water. In many special cases doubtless secondary reactions occur. Some clays even remove the odor and taste from fish oil. Mercaptans and sulfonic acids are removed from petroleum by certain clays. Palm oil is said to be the most difficult to decolorize completely, and crude petroleum is perhaps the easiest.

INVESTIGATION OF COMMERCIAL EARTHS

A list of the principal clays investigated is given below, together with tables of the more significant data obtained, some of which are graphed in the figures.

PRINCIPAL CLAYS EXAMINED

1. Attapulgus, Georgia. Courtesy Attapulgus Clay Company, Philadelphia, Pennsylvania.
2. Macon (Pikes Peak), Georgia. General Reduction Company, Macon, Georgia.
3. Quincy, Florida. "Floridin." Floridin Company, Warren, Pennsylvania.
4. Ocala, Florida. The Superior Earth Company, Ocala, Florida.
5. Crede, Colorado. "Kontak." Peerless Clay & Minerals Company, Chicago, Illinois.
6. San Antonio, Texas. The Standard Fuller's Earth Company, San Antonio, Texas.
7. Olmstead, Illinois. Sinclair Refining Company, Olmstead, Illinois.
8. Aurora, Utah. Western Clay and Metals Company, Aurora, Utah.
9. Aurora, Utah. Western Clay and Metals Company, Aurora, Utah.
10. Death Valley, Nevada. "Palex." D. V. Clay Company, Coen Companies, Inc., Los Angeles, California.
11. Tehachapi, California. "Filtrol." Filtrol Company of California, Los Angeles, California.
12 Chambers, Arizona. "Filtrol." Filtrol Company of California, Los Angeles, California.
13. English Fuller's Earth, Brand XL, purchased.
14. Japanese Acid Clay through Yoshio Tanaka, Tokyo, Japan.
15. D. C. Decomposed Granite, greenish gray, screened, Thirty-third St. and Broad Branch Road.
16. D. C. Decomposed Granite, ash gray, Nebraska Ave. and Rock Creek Ford Road.
17. Weathered Dunite, yellow, Webster, North Carolina. Decomposed olivine.

The clays are listed in Table I in two classes, those for filtering mineral oil, chiefly petroleum lubricants, and those used chiefly for cotton oil, palm oil, fish oil, and lard, which contain OH. The filtering data given in the second and third columns for untreated and acid-treated clays are the volume of oil completely filtered to water-white relative to the volume of the clay filtering it. These

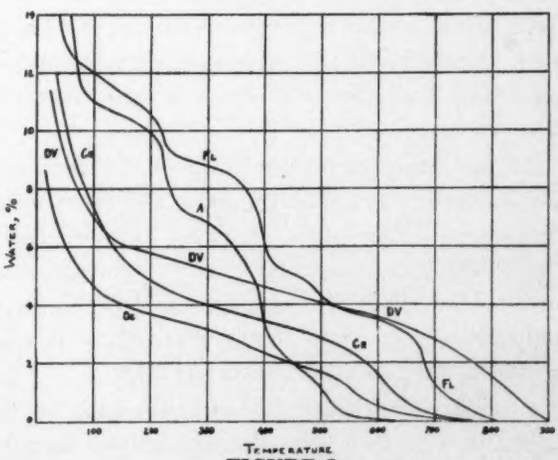


FIGURE 2
Water at Various Temperatures

DV, Death Valley
Cr, Creede
Fl, Floridin
Oc, Ocala
A, Attapulgus

TABLE I. Properties of Bleaching Earths

Clay	Type	White Raw	Bleach Treated	Water Content At: 20% Raw %	80% Raw %	20% Treated %	80% Treated %	Acid Soluble %	Soluble Portion Fe	Al	Ca	Mg	Water Retained At: 50° C. %	100° C. %	200° C. %	300° C %	400° C. %	600° C. %
Attapulgus	Min	0.8	0.5	18.9	32.6	9.3	21.6	18.6	4	4	1	1	14.2	11.0	10.9	6.7	3.5	0.4
Macon	Veg	0.5	0.9	13.2	24.8	7.0	19.8	20.8	6	2	2	Trace	12.8	7.4	5.6	5.2	4.7	2.4
Quincy	Min	0.7	0.6	19.5	29.6	14.8	24.6	25.6	4	3	3	Trace	15.6	12.4	10.4	8.8	6.4	3.5
Ocala	M&V	0.6	0.9	8.9	18.7	3.9	9.8	28.1	3	4	3	Trace	8.1	4.5	3.7	3.1	2.3	0.5
Creede	M&V	0.8	1.2	12.4	23.3	16.4	25.5	11.1	6	3	1	0	10.4	7.2	4.8	4.0	3.4	0.3
San Antonio	Min	0.7	1.1	11.0	21.8	6.9	13.9	11.1	6	3	1	Trace	7.5	5.9	4.7	4.4	3.9	1.5
Olmstead	Min	0.6	0.3	13.9	26.2	14.3	27.3	23.3	7	3	0	Trace	6.9	5.8	4.6	4.1	3.4	1.6
Aurora	Min	1.4	1.2	15.6	30.8	11.3	23.5	10.9	4	3	2	1	10.8	6.1	4.6	4.1	3.6	2.2
Aurora	Veg	1.1	1.2	18.8	28.9	9.8	19.8	9.8	4	4	2	Trace	12.2	6.4	4.5	4.0	3.5	1.4
Death Valley	Min	1.8	1.2	11.6	24.8	7.1	19.2	24.9	Trace	1	1	8	9.2	6.9	5.7	5.1	4.6	3.5
Tehachapi	Veg	1.1	1.1	14.6	22.9	12.3	22.3	13.1	4	4	Trace	2	12.6	8.4	6.2	5.0	4.3	2.1
Chambers	Min	0.6	2.0	26.5	36.5	21.3	44.8	22.6	5	4	1	Trace	14.8	11.6	5.7	5.2	4.7	2.8
English	M&V	1.2	2.0	21.0	29.7	9.3	22.7	19.9	5	4	1	Trace	14.2	8.0	5.3	4.7	4.1	2.2
Japanese	M&V	1.0	1.1	16.1	27.2	7.3	38.7	14.2	3	6	1	0	14.3	7.0	5.2	4.6	3.9	1.7
D. C. Granite	Min	0.0	1.5	17.3	21.9	13.0	26.5	32.6	8	2	Trace	0	7.0	4.5	3.8	3.5	3.3	0.5
D. C. Gray	Min	0.4	1.0	6.3	7.8	4.6	10.5	13.7	5	5	Trace	Trace	5.5	4.6	4.2	3.9	3.8	0.8
Dunite	Min	1.2	1.2	16.1	25.8	12.5	26.6	40.0	5	0	0	5	13.4	9.7	9.1	7.6	6.7	1.3

numbers are only slightly related to commercial value, since it is the yellow and red fractions that are desired in many cases.

The water content of the clay when in equilibrium with air at 20 to 80 per cent relative humidity and about 26° C. are given for both raw and treated clays. These are relative to the ignited weight as base, whereas similar data in Table II are referred to weight at zero humidity (over P_2O_5) as base. Acid treatment in general lowers moisture retention.

The solution obtained by treating each clay 15 hours with hot dilute hydrochloric acid was roughly analyzed for iron, aluminum, calcium, and magnesium, the clay thoroughly washed free from chlorides and again brought to room humidity and weight, the loss in weight being given as acid soluble ranging from 10 to 40 per cent. The soluble portion is chiefly iron and aluminum, but in two cases is iron and magnesium.

In the last six columns (Table I) are given weight percentages of water retained by untreated clays at various temperatures. Since the removal of water not retained at 50° C. is not likely to result in open bonds, and since heating to 200° C. is sufficient to activate a clay, the loss of water between 50° and 200° C. should be a measure of the true absorbing power of clays. The correlation is quite good. The outstanding exception is the Death Valley clay, but this is an impure magnesium silicate.

A few hydration curves are shown in the figures. The weight-humidity curves of Figure 1 are from weights when in equilibrium with carefully checked sulfuric acid solutions in closed vessels. The equilibrium weights taken at eight points are repeatable and reversible, but equilibrium is reached so slowly that only a few complete curves were run on commercial clays.

The weights plotted are related to the base weight at zero humidity, which exceeds the ignited weight by something more than the water of constitution and of crystallization. The interesting part of these curves is the upper end where saturation is approached. Two distinct types are apparent. The complex clays and the potassium chloride ascend steeply to high values as saturation is approached. Such minerals cake on drying from a saturated condition. Clays of this type lose water in a saturated atmosphere when in muddy condition or even when covered with a millimeter of clear water. If a hard dry lump and a thin mud of the same clay are put in the same saturated atmosphere, they approach the same equilibrium water content in a year or two in a very moist but firm condition resembling that of the original wet clay as mined. On the other hand, the amorphous oxides of silicon, aluminum, and iron (see Table II) reach a definite maximum. The acid-treated serpentine gives a curve of the same type, since it has been reduced to open-bonded silica.

TABLE II. Water Content of Clays at Various Relative Humidities

Humidity, %	10	20	30	50	70	80	90	95	98
Quincy	4.2	6.9	8.4	10.2	13.8	17.9	28.6	39.7	46.7
Death Valley	2.1	3.3	4.2	7.0	11.2	14.0	17.0	19.3	21.2
Chambers	7.5	12.8	15.8	19.3	25.0	29.2	34.7	41.1	44.8
Otaylite	6.0	9.1	12.2	18.8	25.1	28.3	33.5	38.4	44.0
Silica gel	3.5	9.0	15.4	30.3	37.4	38.7	39.6	40.0	40.4
KCl	0.0	0.0	0.0	0.0	0.0	0.7	19.7	39.5	....
Serpentine	3.6	6.0	8.4	14.4	24.2	27.8	29.8	31.2	31.3
Al_2O_3(Am)	4.8	6.9	8.4	14.4	24.7	29.8	33.0	34.0	34.4
Fe_2O_3(Am)	3.9	6.0	8.2	13.4	16.1	16.9	17.5	17.6	17.8
"Cr Sil."	2.2	3.2	4.1	6.1	10.0	17.8	38.1	55.2	....

In Table II are given the data of the curves of Figure 1 with some others added for comparison. The Otaylite is a true bentonite having no filtering power even after acid treatment, yet its humidity curve parallels that of the Chambers earth rather closely. The amorphous oxides were prepared in this laboratory. The "chromium silicate" was from a gel formed by chromic acid and is noteworthy for its low retention of water at low and moderate humidities but very high retention approaching saturation. There are no shoulders on any of these curves as there are on some of the weight-temperature curves.

A few hydration-temperature curves are reproduced in Figure 2. The equilibrium is perfectly definite and

reproducible from any given clay stock, but acid treatment or even boiling in water affects some of the curves profoundly. The water is completely reversible up to about 200° C., and irreversible above 600° C. Between these temperatures clays differ considerably in reversibility.

Attapulgus and Floridin are extreme in the amount of water held up to 350° C. and in having pronounced shoulders. Ocala presents the opposite extreme of low, smooth curve. All the other curves lie between Ocala and Floridin and are mostly smooth and regular. Acid treatment of a clay lowers and smooths its dehydration curve to one similar to Ocala.

In Figure 3 are shown thermal dehydration curves of some closely related compounds for comparison. Some of these have been studied by Tanaka ([4]) and others. The iron oxide, permutite, and chabazite curves are smooth and regular, but that of silica gel is distinctly wavy. The decided bow on the aluminum oxide curve between 200° and 400° C. is characteristic. The dehydration curves of many active clays lie near that for silica gel.

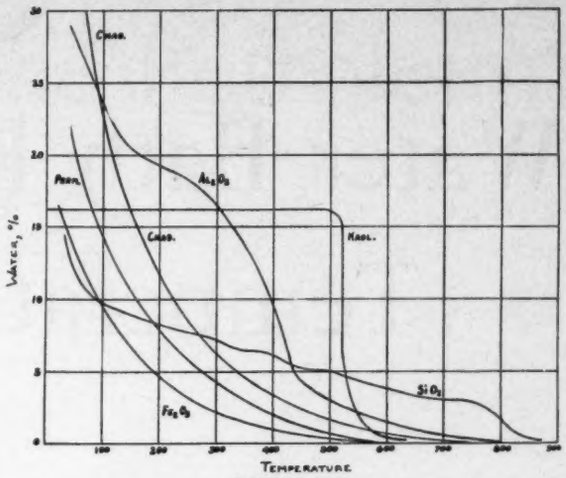


FIGURE 3

Dehydration of Hydroxides

Fe_2O_3 from $Fe(OH)_3$	Permutite
Al_2O_3 from $Al(OH)_3$	Chabazite
SiO_2 from $Si(OH)_4$	Kaolinite

ACKNOWLEDGEMENT

Sincere thanks are due for the whole-hearted cooperation of the many producers of clays for freely supplying materials and information and for permission to visit their mines and plants. The author is greatly indebted to C. S. Ross for much helpful criticism.

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Increasing Octane Values in Gasoline Through Design and Operation of Reforming Units

(Continued from page 285)

Charge Stock		
Gravity	58.7	52.7
I. B. P. °F.	120	198
10%	200	282
20%	230	307
30%	252	322
40%	270	335
50%	289	348
60%	308	363
70%	330	380
80%	364	406
90%	426	453
Octane Number	40	30
Cracked Gasoline		
Gravity	68.5	64.6
I. B. P., °F.	78	78
20%	158	168
50%	216	243
90%	275	313
End Point	297	331
Octane Number	76	76
Residue		
Gravity	3.0	4.0
Flash, °F.	155	150
Fire, °F.	170	175
Saybolt Viscosity at 210° F.	50 Sec.	50 Sec.
Cold Test, °F.	—20	—15

No treating difficulties have been encountered when reforming straight-run gasoline or naphtha. Usually, the product from Pennsylvania gasolines and naphthas have required little or no treatment. The following table shows the tests on cracked unstabilized gasolines made from Pennsylvania naphtha as produced from the unit:

Gravity	68.1
I. B. P.	78°F.
20%	158
50%	216
90%	275
E. P.	296
Octane Number	76
Gum (Copper Dish)	61 mgs.
Vapor Pressure	17.6

Some laboratory results, based on once through operation (without recycling) are shown in Curve No. 1. It will be observed that as the pressure is increased for a given yield, the octane number increases with pressure. Furthermore, at a given pressure, octane number is increased at the expense of yield. These curves are from laboratory data and are intended to show only the trend and not actual yields for various octane numbers. As will be noted these results show considerably lower yields than given previously on commercial plants where recycling is employed.

No attempt has been made in this paper to show how a gas recovery and stabilizing unit, or crude topping unit could be tied in with the reforming unit. However, any one or all of these units can be tied in with the reforming unit in such a way as to meet particular problems; for example. Flow Diagram No. 4 shows a combined crude topping, reforming, gas recovery and stabilizing unit.

Water Bath Keeps Ammonia Temperature Constant

SOME trouble has been experienced by a few refiners in feeding excessive or insufficient quantities of anhydrous ammonia caused by the fluctuating pressures exerted by the fluid in the cylinders when exposed to atmospheric conditions. When temperatures range from the maximum during the hottest part of the day and the minimum during the early morning hours, or when the cylinders have become chilled when left out in the open when it is raining, fluctuations of feed occur. Waste of material is brought about when more than is necessary has been fed to the stream. Incomplete alkalization of the product is experienced when not enough has been fed. Either condition is wasteful. In controlling the feed of ammonia to the system, either manual operation is resorted to, or fluid volume regulators are installed in the line somewhere between the cylinders and the point of entry of the gas into the vapor or liquid stream.

Usually the cylinders when connected to the feed lines are placed in a more or less exposed place where the effect of changing temperature conditions permits the feed of more or less fluid to the stream due to the expansion and contraction of the liquid in the cylinders. To overcome this difficulty, W. F. Irwin, superintendent of Ashland Refining Company's plant at Ashland, Kentucky, places the cylinders in a vat of water so that the change of temperature during the day has little or no effect on the flow of fluid. This vat is large enough to accommodate six cylinders at one time. It was made of steel, welded at the seams to provide a water-tight compartment. It was placed on the ground outside the receiver house. This location makes it convenient for the operators to change loaded cylinders from a truck, or to remove those that have become exhausted. One of the plant water lines is tapped to provide means for filling the vat after the cylinders are placed in position. A drain is welded in the vat in order that the water covering the cylinders can be poured into the plant sewer lines when changing from full to empties.

Ammonia feed is manually controlled, and the controlling needle valves are placed as near the outlet connections on the cylinders as is practicable under the circumstances. Quarter-inch lines lead to the various points of injection. These lines have long easy bends so that they may be swung out of the way when making connections. Quarter-inch Crane needle valves made for ammonia are used in the hook-up. Two of these are placed close to each other with a Marsh ammonia pressure gauge connected between them to show the pressure on the system. The needle valve nearest the cylinder is utilized to control the pressure on the system, while the second valve in the series is used as a fixed adjustable orifice.

When the apparatus was first installed, experiments were carried out using different released pressures against the second needle valve. When the pressure had been found that gave the desired results, all that the stillman or operator need know about the process is the pressure. At a glance he can determine the condition of the system, and when the pressure begins to drop, he may correct and at the same time feed the proper amount of ammonia by opening the pressure control needle valve. He has instructions never to adjust the fixed adjustable orifice except by directions furnished from the laboratory. In using this hook-up with the cylinders in a water bath, consumption of ammonia has been materially lowered.

Water bath utilized to maintain an even temperature on cylinders of anhydrous ammonia while it is being fed to plant vapor lines. Ashland Refining Company, Ashland, Kentucky.

Use of Lime in the Petroleum Refinery

SIDNEY P. ARMSBY
Chemical Engineer

This is the first of a series of technical articles dealing with one of the major chemicals used by the refining industry. The work of Sidney P. Armsby on this subject is one of the most thorough and comprehensive treatises discussing a specific subject that has been compiled.

In the first article the author presents data relative to the proper selection and usages of types of lime for given work, such as neutralizing acid sludge, water treating, grease manufacture. Specifications and characteristics of lime are presented with interpretations of settling rate, available lime content, and tests for determination of both.

Subsequent articles will deal with handling lime in the refinery, and applications of lime in the refinery, in each of which is incorporated much interesting and valuable information on this subject which has not been previously published.

Through several years experience in dealing with manufacture and distribution of lime, Mr. Armsby is peculiarly fitted for this work. He received his B.S. in Chemistry at Pennsylvania State College in 1910. *He was an officer in the Chemical Warfare Service during the World War, in charge of construction and maintenance for the small scale manufacture section. During* 1919-20 *he was in charge of Chemical and Construction Departments for the National Lime Association, from which work he went with Dittlinger Lime Company, New Braunfels, Texas, as chemical engineer for several years. During the past two years he was Service Director for Haden Lime Company, Houston. He is now in consulting service in connection with problems involving the uses of lime.*

GOOD lime, if properly handled and correctly applied, is one of the most useful and economical of all the chemical reagents employed by the up-to-date refiner of petroleum products. Its low cost and its many diverse uses make it a necessity in many departments of every refinery, and a more careful consideration of its merits will, in many cases, reveal unsuspected applications in operations where heretofore its functions have been performed (sometimes perhaps imperfectly) by higher-priced materials. Or it may be that new uses for lime will be developed, with a resultant saving in some detail of operation, or an increase in the life of some piece of equipment or a greater over-all efficiency of a particular production unit.

Any, or all, of these benefits may often be realized if lime is accorded the full measure of recognition it deserves as a strictly high-grade chemical reagent. Of course, in doing this, we must consider it from the same view-point as when discussing any other chemical reagent; namely, its quality and utility. Note that three fundamentals are mentioned: good lime, proper handling and correct application. These naturally indicate the subjects to be discussed in this article, and we shall attempt in succeeding paragraphs to show: First, what constitutes a good lime; second, how it can be handled most satisfactorily and economically; third, what are some of its logical applications in the modern refinery.

WHAT CONSTITUTES A GOOD LIME

Primarily, of course, a good lime is one that is satisfactorily pure, efficient for the particular job in hand, and reasonable in price. Actually, these fundamental requirements are susceptible to various interpretations and shades of meaning—depending upon the use to which the lime is put and the existing knowledge of both the manufacturer and purchaser of the lime as to what constitutes efficiency in any given application to oil refinery processes.

For example: the hydrating operations at most lime plants produce a by-product material known to the lime industry as "tailings". This consists largely of a mixture of hydrated lime and quicklime in varying proportions, but also carries with it a certain amount of other material such as over-burned lime; core (un-burned lime carbonate); sand, clay, and other impurities that were present in the original raw material from which the lime was made. This by-product lime material usually finds a ready sale as agricultural lime, as it contains a fairly high percentage of lime, in a form easily available for neutralizing soil acidity, and is low in price as compared to the purer commercial forms of lime. If this material will neutralize acids in the soil, it is obvious that

Table I
Properties of Typical High-Calcium Hydrated Limes

Sample No.	Specific Gravity	Settling Rate (to 50% volume) Minutes	Fineness (thru 250 mesh) Percent	Available Lime (on non-volatile basis) Percent	Reactivity (converted by sodium carbonate in one hour) Percent
1	2.18	34.0	97.3	82.6	78.9
2	2.18	63.0	98.8	89.0	84.8
3	2.18	76.5	98.2	90.2	86.2
4	2.20	74.0	95.8	89.5	81.1
5	2.21	44.5	99.3	90.3	90.8
6	2.21	43.5	98.1	90.8	79.3
7	....	....	95.0	91.3	88.8
8	2.24	35.0	100.0*	96.5	....
9	2.25	44.5	98.6	75.7	....
10	....	8.0	60.7	19.5	34.1
11	2.35	33.0	97.2	68.5	71.5
12	2.36	7.0	91.4	49.7	51.8
13	2.48	44.0	95.5	49.6	47.5
14	2.56	53.0	97.5	46.0	45.7

*100% through 325 mesh

it can be used also to neutralize acid refinery wastes and that it may offer an economical means of treating plant effluents so as to solve troublesome problems, either practical or legal. The value of such "tailings" for this particular application will depend upon two things—how much acid a given quantity of it will neutralize, and what it will cost delivered to the point of application. The lime manufacturer will, of course, be glad to co-operate in establishing values based on the chemical analysis of the material and the costs of handling and, with such values correctly determined, this grade of lime virtually becomes 100 per cent efficient for this application.

WATER SOFTENING

If, however, such a by-product material had been proposed for use in softening the boiler water used at the refinery power house the considerations involved would be altogether different and it would not be acceptable. The large percentage of impurities present might alone be sufficient to condemn it. Other factors, however, are still more important in this case and are worthy of special mention in this discussion. When evaluating limes to be used for water treating it should be borne in mind first of all that the lime will be added to the raw water in the form of a suspension and not as a solution, lime being soluble in water only to the extent of about one part in 1700. This suspension, or milk of lime, should be of such a character that the suspended particles of lime (in the form of calcium hydroxide) with become thoroughly and completely dispersed throughout the volume of the water being treated, as this is the only way in which contact can be made between the molecules of lime and those of the dissolved compounds with which it is intended to combine or react. Hence it is obvious that for any given degree of purity, the smaller the lime particles, the more completely they are capable of being utilized in the reaction chambers, other conditions being favorable. Here, then, we find that a physical property of the lime may be equally as important as its chemical analysis in determining its value for certain operations.

SETTLING RATE

To emphasize this point, discuss the "settling rate" of the lime, or the time required for the particles of lime to settle out of suspension in the reaction or sedimentation basins, after agitation has been stopped. (This settling rate should not be confused with specific gravity, as two limes of almost identical specific gravity may have very different rates of settling, as shown in the list of typical hydrated limes in Table I.)

Suppose that we have calculated from chemical analyses that one million gallons of water will be correctly treated by the addition of 250 pounds of a certain grade of hydrated lime. This means that, in order to complete the necessary reactions, each pound of lime must first be evenly dispersed (by means of agitation) throughout 4000 gallons of water, after which the individual solid particles of lime must float about more or less freely for a length of time sufficient to allow them either to be dissolved by the water or to react with other compounds already in solution.

If, instead of remaining in suspension, the lime particles settle out before complete solution or reaction has had time to take place, the "settling rate" is too rapid and a part of the lime (otherwise reactive) will accumulate as a sediment in the bottom of the tank and be of no value to the process. Such a condition would mean that excessive amounts of lime would have to be added in order to effect satisfactory treatment of the water, and would be another excellent demonstration of the fact that both physical properties and chemical analysis should be considered in determining the efficiency of chemical lime.

The standard method of determining the settling rate of lime was developed in the laboratory of The National Lime Association, Washington, D. C., and is carried out as follows:

For quicklime, carefully slake 7½ grams with sufficient distilled water to make a thin slurry. For hydrated lime, thoroughly mix 10 grams with water to the same creamy consistency. In either case, cover the vessel containing the slurry and let it stand for at least 12 hours, preferably over night.

Wash the slurry into a 100-c.c. graduated cylinder approximately 2.5 centimeters in diameter; make up to the 100 c.c. mark with distilled water; shake vigorously to completely disperse the lime; set aside on a level surface, and note the time.

As the lime settles out of suspension it shows a sharp line of demarcation between the clear lime water

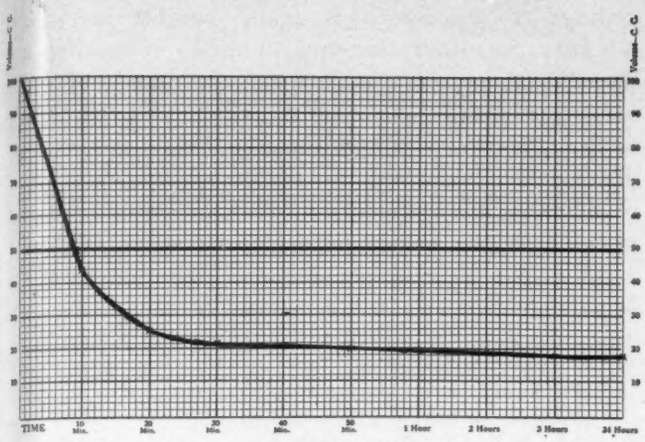


FIGURE 1

Rate of settling, sample quicklime No. 1. Settling rate, nine minutes; final volume, 18 per cent.

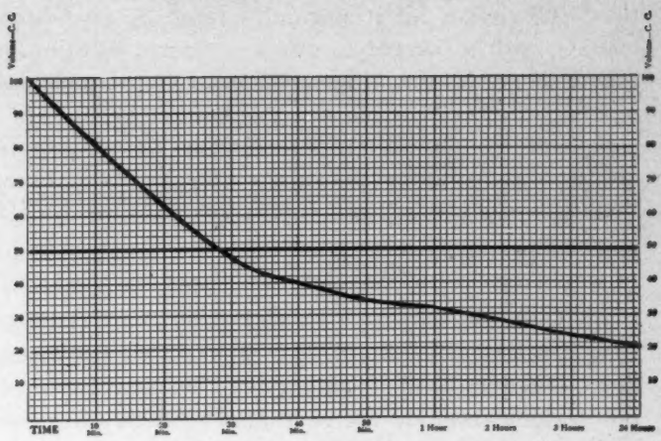


FIGURE 2

Rate of settling, sample quicklime No. 2. Settling rate, 28 minutes; final volume, 20 per cent.

solution and the still unsettled lime, and the position of this line may be recorded at such time intervals as may be desired, being sure, however, to note the time required for the lime to settle to the 50-c.c. mark (50 per cent of the original volume), and also noting the amount of settling at the end of 24 hours.

The time required to settle 50 per cent is called the "settling rate" and the volume at the end of 24 hours is called the "final volume."

Note—Be sure to use graduated cylinders of the same inside diameter in making all tests.

While this is purely an arbitrary test, its use gives reliable information as to the settling properties of different limes and, if results are consistently recorded, will be found of very practical use in determining their relative merits for certain process applications. Figures 1, 2 and 3 illustrate the use of a chart designed by the writer for graphically recording such data, and also indicate some of the variations that are encountered.

AVAILABLE LIME CONTENT

The foregoing discussion of the "settling rate," and its influence in determining the value of lime for water treating or other uses, should not be interpreted as meaning that any arbitrary limit of settling time can be set up and applied to all brands of lime that may be offered for chemical process work. This is because a too rapid settling rate for one lime may be perfectly satisfactory for some other material of almost identical "available lime" content.

The term "available lime" designates that portion of any lime (either quicklime or hydrated lime) which is readily soluble in water or other reaction media—thus becoming easily available for chemical reaction. The difference between available lime and total lime shows us the percentage of the whole that is combined, either physically or chemically, with impurities or is in such a physical condition that it is unavailable for the purpose in hand.

Current specification C-25 — 29 (The American Society for Testing Materials) gives the standard laboratory method for determining available lime, and this is generally accepted as being the correct measure of the reaction efficiency of any chemical lime—frequently being made the basis of purchase specifications. It should be pointed out, however, that this method of testing fails to take account of the time element involved when the lime is used in commercial work, whereas the operating superintendent wants to know not only how much available lime is present, but also how quickly it is available. Two factors will influence the time required for all of the available lime to become effective, and these are particle size and settling rate, both previously mentioned.

Just as a small lump of sugar will dissolve more quickly than a large one, so a small particle of lime in suspension will be dissolved (or be reacted upon) in less time than a larger particle, even though both may be completely soluble. It is evident, therefore, that the "time of availability" of any lime bears a direct relation to its particle size.

Similarly, the speed with which a given lime settles out of suspension after agitation has been stopped, has its influence upon the amount of lime that will become available in any given length of

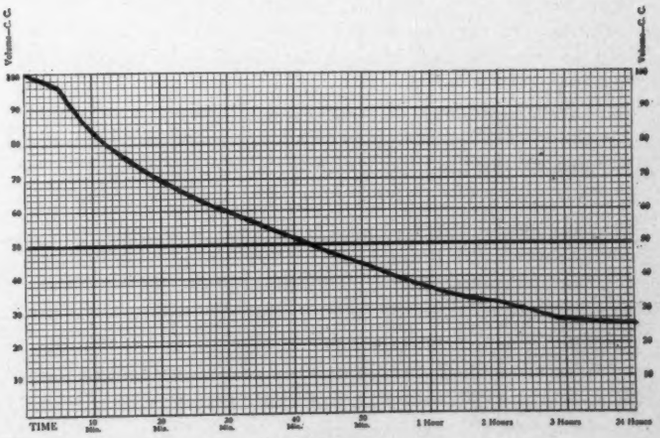


FIGURE 3

Hydrated lime No. 47 (composite sample). Settling rate 42 minutes; final volume, 26 per cent.

time. Obviously, if it normally requires an hour's contact with a solvent to effect complete solution, a lime that settles out of suspension in 30 minutes can not be expected to yield the full benefit of its available lime content. If, however, only 20 minutes is required for complete solution of the available lime, then a 30-minute settling rate is no handicap on its efficiency.

IMPROVED TEST

These considerations, and a comparison of the settling rate and available lime content of the specimen limes listed in Table I emphasize the importance of the statement made above that a settling rate too rapid for one lime may be perfectly satisfactory for another of almost identical composition. It appears from these facts that, when writing purchase specifications designed to insure the quality of "chemical lime," care should be taken to establish the proper relation between "available lime content"; "settling rate"; "reaction rate," and "fineness."

This may be done by making use of the standard laboratory proceedures prescribed by The American Society for Testing Materials or The National Lime Association, designating such requirements in each case as will be fair to both the manufacturer and consumer of the lime. Of perhaps the preparation of such specifications may be simplified by taking advantage of a simple laboratory method of testing the availability of lime which was developed by The International Filter Company of Chicago, Ill., for use in classifying various commercial brands of hydrated lime now on the market.

This test is designed to show the percentage of calcium hydroxide alkalinity developed in solution when a sample of lime is agitated for different lengths of time with an excess of pure distilled water —the conditions approximating those which exist in a commercial treating plant. The detailed instructions for making the test are as follows:

> "Add 0.4 gram of (hydrated) lime to 200 c.c. of carbon dioxide-free (distilled) water in a 500 c.c. bottle. 200 c.c. more water is then added and the bottle corked and placed in a shaking machine and shaken for 10 minutes. At the end of this time a sample of about 100 c.c. is removed and filtered, carbonation being guarded against, 50 c.c. of the filtrate is titrated with 1/10 normal hydrochloric acid, using phenolphthalein indicator to the disappearance of the red color and then methyl orange to the final end point. The hydroxide alkalinity is calculated from these two figures, in terms of c.c. of acid used, and this figure is then multiplied by 7.4 which gives the percentage of calcium hydroxide.
>
> "Immediately after the 10-minute sample is withdrawn, the remainder of the original solution in the bottle is again shaken for an additional 50 minutes, making a total of 60 minutes. A second sample is then taken and the percentage of calcium hydroxide determined in the same manner."

It will be appreciated that this simple method gives a pretty accurate determination of the percentage of lime which is really soluble in water, whereas the other standard methods of testing are likely to be more valuable when the lime is actually used to neutralize an acid, or when it is fed into a solution in which all of the available lime will be utilized; for example, in removing hydrogen sulphide from crude naphtha, or in the manufacture of grease. It is worth nothing also that this test method eliminates any variations due to differences in particle size or settling rate when comparing two different limes, as settling is avoided and complete dispersion is assured throughout the test period.

It would be highly desirable for oil refinery laboratories, in cooperation with lime plant chemists to develop a combination method whereby the scope of the above outlined test could be broadened to include the test of samples at various intermediate time intervals between zero and 60 minutes, and also to include testing in other reaction media besides water. A comparison of such test results with those obtained by A. S. T. M. methods would give reliable data as to the real availability of any lime for practically any oil refinery process. Such data, supplemented by complete chemical analysis and determinations of settling rate and particle size, would supply all the information needed as the basis of a complete set of purchase specifications covering lime for use in every department of the refinery. Specifications built up in this manner would assure for each department a lime that would be economical and efficient for its use, and would avoid the possibility of unjustly penalizing some inherent property in any particular brand of lime.

PRINCIPLES GENERALLY APPLICABLE

While the discussion thus far has centered principally around the properties that govern the choice of a lime to be used for water softening, this was done for the purpose of illustrating fundamental principles and because detailed data were readily available covering the particular points mentioned. The same general considerations may be applied to either quicklime or hydrated lime for use in any process operation employed in the manufacture of petroleum products, merely by making suitable variations in the details of the specifications drawn up for separate departments. It is only necessary to fit the lime specification to the job in hand, bearing in mind the fact that certain properties of any given lime may be objectionable in one process; beneficial in another, and of no significance in still a third. If these facts are recognized by both the oil refiner and the lime manufacturer, it will enable the producer to furnish the correct grades of lime and will assure to the consumer the maximum of efficiency in each of his separate applications of the lime.

A few brief illustrations will demonstrate the truth of the above statements:

(1) In a lime to be used for neutralizing acid wastes it makes no difference whether it be a high-calcium or high-magnesium lime, or whether its impurities are of a gritty character, only its power to neutralize acids being of primary importance.

(2) For water treating, however, magnesium oxide is decidedly objectionable, not only because of its own undesirable effects but also because it offsets the value of more than its own weight of calcium oxide. Gritty impurities, on the other hand, are usually inactive so far as chemical reaction is concerned and are considered simply as so much inert material, although it is possible in some cases for reasonable amounts of such material to assist in sedimentation and removal of precipitated, or flocculated compounds produced by reactions taking place during the treating process.

(3) For grease making the lime should be entirely free from any gritty material whatever, as the least trace of grit in the finished grease may destroy its value. Magnesium oxide, however, may or may not be harmful, depending upon the effect which magnesium soaps may have on the quality of the finished product.

(4) The settling rate of lime has been shown to have an important bearing on its efficiency for water treating, but in either grease making or acid neutralizing there is usually sufficient agitation provided to overcome any tendency of the lime to settle out before the reaction is completed.

(5) Small percentages of certain elements present in lime (such as manganese, phosphorus, sulphur, etc.) may cause chemical reactions or catalytic effects that will be either harmful, beneficial or of no importance in various processes.

Just as it is easy to utilize a water-fall as a source of power, while it requires the consumption of power to reverse the flow by lifting water against the force of gravity, so it is much easier and more economical to make proper use of the chemical and physical properties of lime than to try to fight against them. Fit the lime to the job and the job will be better done, especially since it is often possible to secure from the same plant several different grades of lime, each of which may be suited to a definite requirement or a specific process.

PURCHASE SPECIFICATIONS

A purchase specification for chemical lime is similar to a contract between a property owner and the contractor who erects an office building. In each case the contractor is guaranteed a certain compensation for a specified quantity and quality of work accomplished, and the purchaser is guaranteed a certain result for a specified expenditure.

The fairness, to both parties, of properly prepared lime purchase specifications is beyond question. If a ton of one lime will satisfactorily treat two per cent more water, oil or naphtha than the same quantity of another lime, or if it will produce a two per cent improvement in the quality of a given yield of grease, then it is worth at least a two per cent premium—especially when we consider that no extra freight or handling charges are necessary in order to secure the extra benefits. Having once established a fair contract price for a specified quality of lime, it is only necessary to incorporate in the specification, or contract, a schedule of bonuses and penalties based on definite percentages of the contract price for correspondingly definite percentages of quality above or below the guaranteed quality.

PREPARING SPECIFICATIONS

In preparing a purchase specification for lime, the first thing to be considered is the relative importance of its various chemical and physical properties, as they affect the process in which the lime is to be used. If intending to cover lime for neutralizing acid plant effluents, where agitation is sufficient to overcome settling tendencies, we may limit the specifications to a simple contract calling for the payment of so much money for a given unit of active basic material capable of combining with the acids involved. For other uses, however, we should list such considerations as available lime; fineness; rate of reaction; settling rate; percentage of impurities (either separately or collectively); physical character or chemical reactions of impurities, and degree of re-carbonation in transit or storage, assigning to each one its proper importance and eliminating those which have no bearing on the case in hand.

Having clearly in mind the functions to be performed by the lime, and having determined by suitable laboratory tests the properties or characteristics which may limit its efficiency, we are in position to set up a finished specification that will adequately protect both buyer and seller and insure the efficiency of any given process operation. Two such purchase specification forms are suggested, as follows:

Lime Specification No. 1

(Bulk quick-lime for water softening)

(a) Guaranteed Analysis:

Silica . . . . . % maximum
Iron Oxide . . . . . % maximum
Aluminum Oxide . . . . . % maximum
Magnesium Oxide . . . . . % maximum
Carbon Dioxide . . . . . %
Calcium Oxide (total) . . . . . % minimum
Calcium Oxide available in——minutes . . . . . %
Settling Rate (50% volume) . . . . . ——minutes, minimum

(b) Sampling and Testing:

As cars are loaded, a composite sample shall be taken according to current specifications of The American Society for Testing Materials (Designation C 50-27), and one portion of said sample shall be delivered to the purchaser and one portion retained by the shipper. The purchaser shall also take samples by the same method upon arrival of

the lime and the analyses of these samples shall govern in the settlement of accounts, as provided for in following sections of this contract specification. All analyses shall be made according to the methods prescribed by The American Society for Testing Materials, or such other methods as are stated in detail below. (State here details of other test methods to be used.)

(c) Bonuses and Penalties:

The purchaser will pay bonuses and the shipper will pay penalties according to the following schedule covering any carload lot which does not conform to the above guaranteed analysis.

1. *Silica, Iron Oxide and Aluminum Oxide*—Penalty of——cents per ton for each one per cent or fraction thereof by which the total of these combined impurities exceeds the guaranteed maximum of——per cent.

2. *Magnesium Oxide*—Penalty of——cents per ton for each one per cent or fraction thereof in excess of the guaranteed maximum of——per cent.

3. *Carbon Dioxide*—Bonus and penalty of——cents per ton for each one per cent (or one-half per cent) by which the carbon dioxide content is below or above the guaranteed figure of——per cent.

4. *Total Calcium Oxide*—Penalty of——cents per ton for each one per cent below the guaranteed figure of——per cent.

5. *Available Calcium Oxide*—Bonus and penalty of one per cent of the contract price per ton for each one per cent above or below the guaranteed figure of——per cent available in——minutes; and a further bonus of——cents per ton for each——minutes by which the time required for the guaranteed ——per cent of calcium oxide to become available shall be decreased, below the stated time of——minutes.

6. *Settling Rate*—Penalty of——cents per ton for each——minutes by which the settling rate shall fall below the guaranteed minimum of——minutes; *except* in the event the time required for availability of the above-guaranteed——per cent of calcium oxide remains less than the settling rate, in which case this penalty shall not be applied.

(d) Terms of Settlement:

The carload lot shall be used as the basis of accounting, and each carload lot shall be paid for by the purchaser at the full contract price and on such terms as shall be mutually agreed upon in writing by both purchaser and seller, such written agreement being attached to and made a part of this contract. The bonus and penalty account shall be kept as a separate financial transaction, bonuses and penalties being determined by analysis of each carload lot as received, and accounts being balanced at such times and in such manner as shall be mutually agreeable to both parties concerned.

(e) Disagreements or Complaints:

In event of any material disagreement between analyses reported by the laboratories of the seller and the buyer, the chemists making these analyses shall confer to determine whether any errors have been made and if so, to correct them. If their differences cannot be reconciled, the matter may be submitted to a disinterested laboratory for decision.

(Note: No guaranteed maximum or penalty for calcium sulphate has been included in this specification, because most good grades of lime are sufficiently low in this impurity so that it need not be considered. If excessive amounts should be present, however, it would tend to harden the water being treated.)

A similar specification for hydrated lime could be written by making a few changes in the wording of the above, so as to cover "calcium hydroxide" instead of "calcium oxide" and introducing guarantees as to fineness if desired. On the basis of such a specification, it will be seen at a glance that hydrated limes 9 to 14, inclusive, in Table I. would be entirely unsatisfactory, and that No. 1 would be doubtful until further tests had been made.

Lime Specification No. 2

(Hydrated lime for cracking stills)

(a) Substitute "calcium hydroxide" for "calcium oxide" (both total and available.)
Make suitable change in the settling rate guarantee, as tests indicate justifiable.
Eliminate time factor under "available lime."
Add guaranteed maximum for free moisture.
Add guaranteed minimum fineness.
(Other guarantees same as Spec. No. 1.)

(b) (Same as in Spec. No. 1.)

(c) Under "5" change to "calcium hydroxide" and eliminate time factor.
Under "6' eliminate the "exception."
Add penalty for excess moisture.
Add bonus and penalty covering "fineness."
(Other sections same as Spec. No. 1.)

(d) (Same as in Spec. No. 1.)

(e) (Same as in Spec. No. 1.)

By using some such basic scheme as that indicated above it is a simple matter to prepare purchase specifications, or contracts, for chemical lime covering every refinery use, all that is required being correct information as to the functions performed by the lime and a proper spirit of co-operation and fair play between the lime manufacturer and the petroleum refiner.

SUMMARY

In summing up this discussion of what constitutes a good lime for use in the modern petroleum refinery, it may be stated that, for any particular refinery operation, a good lime is one that possesses such of the chemical and physical properties outlined in this section as are required for the proper functioning of the process in which it is to be used. We have shown that a certain type of lime may be quite inefficient for one purpose and very excellent for another, and that the correct utilization of any particular grade of lime is, in the last analysis, the actual measure of its quality.

This is the first of a series of three articles by Mr. Armsby. The second section outlines various types of equipment for handling lime in refineries, different limes for different purposes in the refining process, and safety devices and measures proper to handling the material. This will appear in an early issue.

The Rectification of Natural Gas Condensates

I. N. BEALL

THE accompanying discussion is part three of a series of articles dealing with the rectification of natural gas condensates. In this work the writer interestingly presents data calculated to be of assistance in the separation of individual hydrocarbons, or fractions containing two or more constituents. He states, for example, for separation of the mixture (distillate from the stabilization of wild natural gasoline) into its components other than methane, perhaps the logical procedure would be to separate the methane together with some ethane and propane in one column, send the fractionated residue to a second column for ethane separation, to a third column for propane separation, and to a fourth column for final separation of isobutane and butane. Equations and charts of workable value accompany the discussion.

THE continuous rectification of any liquid mixture of two or more compounds depends upon partial vaporization and partial condensation. The vapors from the liquid mixtures are richer in the more volatile constituents than the unvaporized portions and the condensates are richer in the less volatile components than the vapor from which separated.

The fact that a mixture consists of a great number of components, all differing in vapor pressure characteristics, in no way changes the principles involved but it makes the mathematical analysis more difficult. In mixtures of non-associated liquids such as those formed by the natural gas hydrocarbons, Raoults Law enables the prediction of what the vapor composition will be from a knowledge of the composition of the liquid mixture. Inasmuch as the composition of the total liquid and vapors in a rectifying column are dependent upon the feed and the reflux, it is apparent that analyses of both should be available.

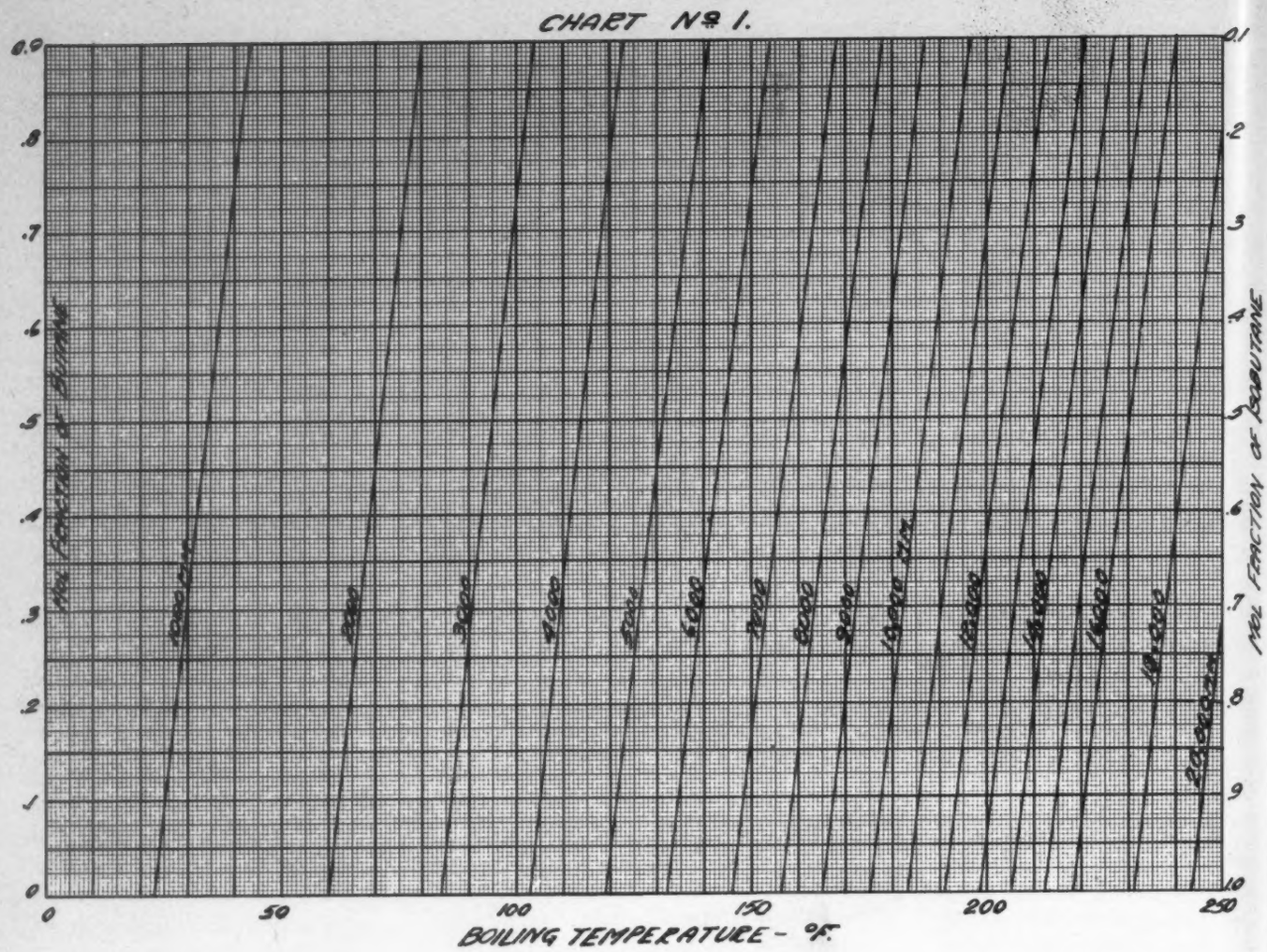
For every separation of two or more components by fractional distillation there is a minimum reflux ratio. The closer this separation is to be, the higher will be the amount of reflux required, other factors remaining equal. The minimum theoretical reflux ratio is for a column containing an infinite number of perfect plates, an impossible condition. The concept, however, is useful as the true or actual reflux ratio lies somewhere between the minimum and that of total reflux where no vapors pass from the system.

Although the graphical method of analysis such as that used by McCabe and Thiele may not apply to all mixtures, an understanding of such charts and their basis of construction gives the best obtainable visualization of the principles of fractionation. In natural gasoline fractionation, for example, where the point of separation is between isobutane and butane or propane and butane, graphic analysis is a valuable aid as a means of rapid analysis.

The objective in all cases narrows down to two constituents. If these are separated by fractionation the less volatile will be in the residue and the more volatile will be in the distillate. That is to say, if there is perfect separation between isobutane and butane by rectification of a complex natural gas condensate, it is highly probable that all the propane, ethane and methane will be included with isobutane in the overhead distillate and that all the pentanes, hexanes, heptanes, etc., will be included in the residue or kettle product.

In a mixture of two components such as, for example, isobutane and butane, the boiling point of the mixture is dependent upon the proportion of each in the mixture and the pressure on the system. No separation is possible above the critical temperature as both liquid and vapor phase are essential to separation. The closer the approach to the critical temperature the more difficult separation becomes. It is therefore advisable to keep the operating pressure as low as is consistent with the cooling or condensing medium available. No high pressure columns would be in use were it not for the fact that low temperatures are expensive to maintain. The volatility ratio increases from the critical point down to limits of vacuum.

In mixtures of the saturated hydrocarbons, the



highest boiling point would be slightly lower than that of the highest boiling point compound in the mixture and the lowest boiling point would be a trifle higher than that of the lowest boiling point hydrocarbon. For binary mixtures, the boiling point for every composition can be closely approximated by

$$x_1 T_1 + x_2 T_2 = \text{Boiling Point}$$

where x_1 and x_2 are the respective mol fractions and T_1 and T_2 are the absolute temperatures taken from the vapor pressure curves.

For example mixtures of butane and isobutane at 5000 millimeters absolute having the following composition: 0.1, 0.2, 0.3, 0.4, 0.5 . . . 0.9 mol fraction of isobutane.

$T_1 = 119°$ F. $+ 460 = 579°$ F. Abs.
$= $ Temp. of Isobutane corresponding to 5000 mm.

$T_2 = 143°$ F. $+ 460 = 603.0°$ F. Abs.
$= $ Temp. of Butane corresponding to 5000 mm.

The corresponding temperature in degrees Fahrenheit is found by subtracting 460 from the last column. See Chart No. 1 for values at other pressures. The vapor composition on liquid composition curve can now be calculated as in Table II.

TABLE I

Mol. Fraction Isobutane	Butane	$x_1 T_1$	$x_2 T_2$	$x_1 T_1 + x_2 T_2$
0.0	1.0	0	603	603.0
0.1	0.9	57.9	542.7	600.6
0.2	0.8	115.8	482.4	598.2
0.3	0.7	173.7	422.1	595.8
0.4	0.6	231.6	361.8	593.4
0.5	0.5	289.5	301.5	591.0
0.6	0.4	347.4	241.2	588.6
0.7	0.3	405.3	180.9	586.2
0.8	0.2	463.2	120.6	583.8
0.9	0.1	521.1	60.3	581.4
1.0	0.0	579.0	00.0	579.0

The vapor pressures were read directly from the chart so that there is some inaccuracy as evidenced by the fact the sum per cent of isobutane and butane in the last two columns varies from 100 per cent. The agreement in general however is good and serves as a check on the calculations.

When plotted in the form of a smooth surve (see Chart No. 2) the inaccuracies become negligible.

The data in Tables I and II are sufficient for a

TABLE II

$P\ \pi = 5000$ mm.

$x_1T_1 + x_2T_2$	T°F.	P_1 — mm	P_2 mm	P_1x_1	P_2x_2	$\frac{100\ P_1x_1}{\pi}$	$\frac{100P_2x_2}{\pi}$
603.0	143.0	6800	5000	0	5000	0	100
600.6	140.6	6500	4800	650	4320	13.0	86.4
598.2	138.2	6400	4700	1280	3760	25.6	75.2
595.8	135.8	6350	4600	1905	3220	38.1	64.4
593.4	133.4	6125	4350	2450	2610	49.0	52.2
591.0	131.0	5800	4200	2900	21.00	58.0	42.0
588.6	128.6	5700	4100	3420	1640	68.4	32.8
586.2	126.2	5450	4000	3815	1200	76.3	24.0
583.8	123.8	5300	3800	4240	760	84.8	15.2
581.4	121.4	5100	3700	4590	370	91.8	7.4
579.0	119.0	5000	3600	5000	0	100.0	0.0

graphical analysis of the plate and reflux requirements for a column operating at the pressure given. There is a difference of only 24° F. between the boiling points of isobutane and butane at 5000 mm. absolute (96.7 lbs. abs.). The volatility ratio is between $\frac{5000}{6800} = 0.736$ and $\frac{3600}{5000} = 0.720$ between the temperatures given in Column 2 of Table II. The equilibrium temperature difference between 91.8 per cent isobutane vapor mixture and 100 per cent isobutane is 2.4° F., showing that a close temperature gradient per plate will be necessary for separation of these two hydrocarbons from their mixtures and also that a relatively high reflux ratio will be required.

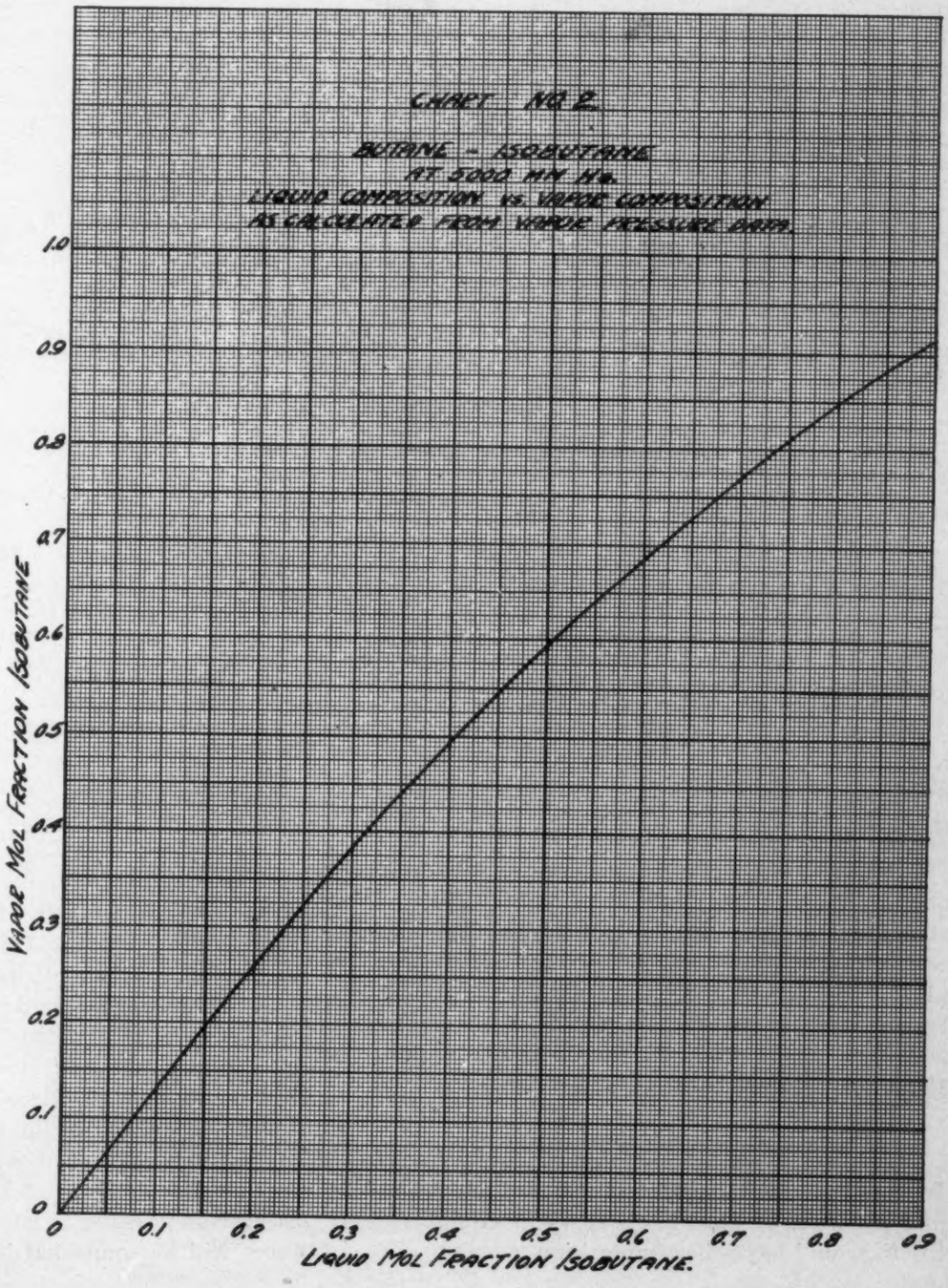
This much at least is apparent from an inspection of the calculated data and the equilibrium curve. A graphical analysis based on the derived data will give the number of theoretically perfect plates necessary for the separation and the minimum reflux ratio. However, if the effective condenser temperature obtainable is 80° F., the operating pressure may be set at 2800 mm. absolute (54.2 lbs. abs.) and the boiling temperature difference between isobutane and butane will be at that pressure will be 102 — 80 = 22°F. The maximum and minimum volatility ratios will be

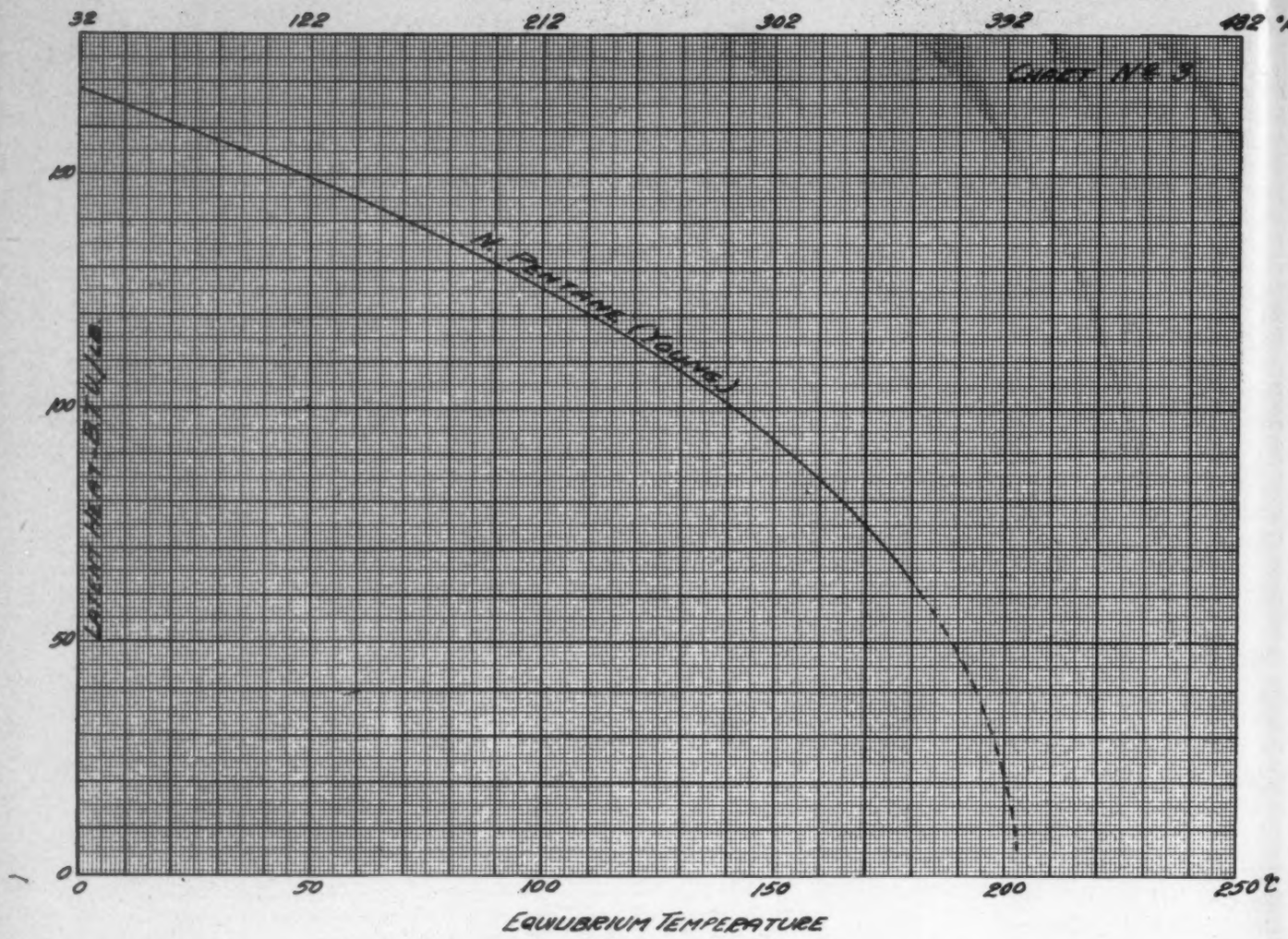
$$\frac{1900}{2800} = 0.679$$

and

$$\frac{2800}{3950} = 0.709$$

which is a quantitative index of the ease of separation at 500 mm. operating pressure and 2800 mm. operating pressure. The lowest volatility ratio is to be preferred from the viewpoint of the number of plates, but closer reflux temperature control is required for the same degree of separation. In actual practice with the present development in temperature control instruments, the higher pressure would be pre-





ferred as the lag between high and low should not exceed over 0.5° F. in the case given.

The equation

$$x_n \frac{P_n V_n}{\pi} = x_{n+1} O_{n+1} + x_d D_1$$

may be used to calculate the number of plates above the feed for any of the operating pressures chosen for isobutane—butane fractionation and

$$x_{m-1} O_{m-1} = x_m \frac{P_m V_m}{\pi} + x_w R.$$

of plates below the feed.

PROPANE—ISOBUTANE MIXTURES

High operating pressures are required for propane and isobutane separation than are required for the separation of isobutane — butane mixes but otherwise the fractionation is simpler and requires fewer plates. For example, at 5000 mm. the corresponding temperature on the propane vapor pressure curve is 54° F. At 54° F. the vapor pressure of isobutane is 1800 mm. or a volatility ratio of

$$\frac{1800}{5000} = 0.360.$$

In a liquid mixture of 30 mol per cent butane and 70 mol per cent propane the vapors in equilibrium at 54° F. would have the composition

$$\frac{.3 \times 1800 \times 100}{4040} = 13.35 \text{ \% isobutane and}$$

$$\frac{.7 \times 5000 \times 100}{4040} = 86.65 \text{ \% propane.}$$

Rt 54° F. effective condenser pressure for the column, the highest operating that would be carried could not be greater than 5000 mm. absolute. However, at a temperature of 90° F., 8400 mm. would be required for the condensation of a pure propane distillate. Let it be supposed that this operating condition exists and that a kettle temperature 50° F. higher is selected, at 140° F. the vapor pressure of propane is found to be 15,525 mm. and that of isobutane 6,550. Assuming that the pressure drop through the column is negligible in comparison to the operating pressure, the vapor pressure of the kettle product must be in slight excess of the operating pressure in order to boil and therefore must consist of a mixture of the two constituents. However, at 160° F., the vapor pressure of isobutane is 8,400 mm. and therefore is equal to the operating pressure. If a clean separation of the two constituents is desired, the kettle temperature should be maintained as near as possible to 160° F. and the condenser temperature as near as possible to 90° F. Actually both temperatures will be somewhat less than 160° F. and 90° F.

as perfect separation is possible only in theory. A carefully controlled heat input would be required not in excess of that required for vaporization and expulsion of the propane vapors, that necessary for revaporization of reflux, that lost from the apparatus, plus whatever was necessary for butane vaporization in excess of that required for propane vaporization. Heat also will be necessary to bring the temperature of the liquid mixture to the boiling point.

SEPARATION FROM DISTILLATES

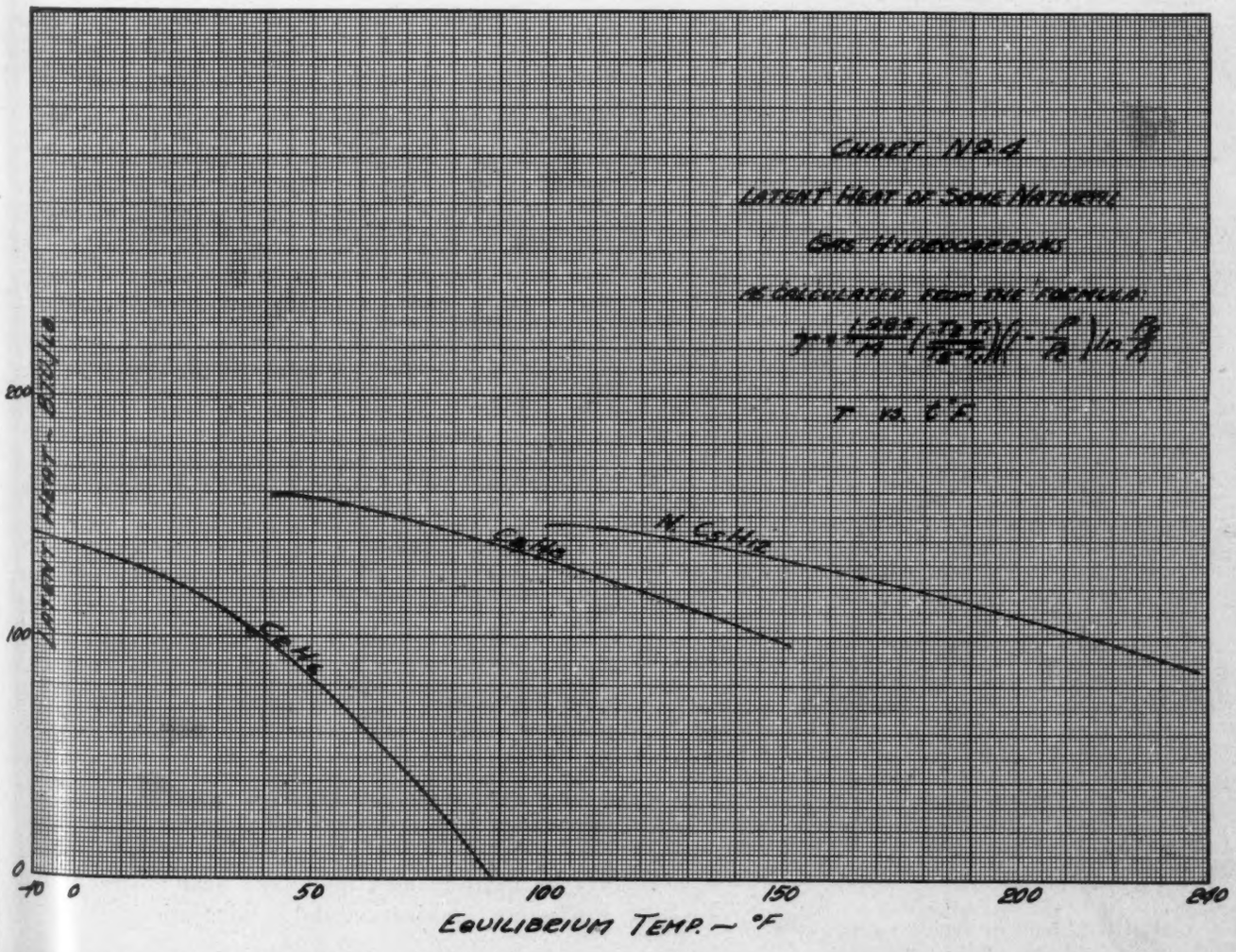
The distillate from the stabilization of wild natural gasoline will consist, as a rule, of a mixture of five components; namely, butane, isobutane, propane, ethane and methane together with traces of the higher hydrocarbons, the amount depending upon the closeness of separation. From this distillate which may be a product of partial or total condensation, it may seem desirable to separate individual hydrocarbons, or fractions containing two or more constituents. For separation of the mixture into its components other than methane, the logical procedure would be to separate the methane together with some ethane and propane in one column, send the fractionated residue from this column to a second column for ethane separation, to a third column for propane separation, and to a fourth column for the final separation of isobutane and butane. Four columns in all would be required for the separation in addition to that needed for the stabilization of the natural gasoline. For warm weather operation, artificial refrigeration will be needed for the first two columns operating on natural gasoline distillate, water would serve as the condenser cooling medium for the two final columns for the separation of porpane, iso-butane, and butane. Let us assume that the distillate from the gasoline stabilizing column has the following composition:

Component	Mols	Mol %
CH_4	12	23.0
C_2H_6	15	28.9
C_3H_8	11	21.2
Iso C_4H	6	11.5
N C_4H	8	15.4
Total	52	100.0

The first distillate from this distillate may be taken as

Component	Mols	Mol %
CH_4	12.0	43.4
C_2H_6	15.0	54.4
C_3H_8	0.6	2.2
Total	27.6	100.0

Suppose that an effective condenser pressure of —4°F is available by brine circulation. At this tem-



perature the vapor pressure of ethane is found to be 14.02 Atm. and that of propane 2.37 Atm.

Then $p_2 = 14.02$ $x_2 = 0.544$
and $p_3 = 2.37$ $x_3 = 0.022$
But equating to unity
$x_2 + x_3 = 1$
Therefore

$$\left(\frac{0.434}{14.02} + \frac{0.22}{2.37}\right) = 1$$

$= 24.9$ Atm. Abs.

The column operating pressure is therefore set as 24.9 atm. absolute or $23.9 \times 14.7 = 351$ lbs. gauge. Taking the extrapolated vapor pressure of methane as 200 atmospheres, the composition of the condensate may be calculated by methods previously illustrated.

STEP 1

	$= 24.9$ Atmospheres	$T = -4°F$
$P_1 = 200$	$\frac{P_1}{\pi} = 8.03$	$1 - \frac{P_1}{\pi} = -7.03$
$P_2 = 14.02$	$\frac{P_2}{\pi} = 0.563$	$1 - \frac{P_2}{\pi} = 0.437$
$P_3 = 2.37$	$\frac{P_3}{\pi} = 0.095$	$1 - \frac{P_3}{\pi} = 0.905$

STEP 2

Try $L = 10$

(1) $$\frac{160\ x}{L} = \frac{43.4}{803 + 10\ (-7.03)} = 0.0592$$

(2) $$\frac{100\ x_2}{L} = \frac{54.4}{56.3 + 10\ (0.437)} = 0.8962$$

(3) $$\frac{100\ x_3}{L} = \frac{02.2}{9.5 + 10\ (0.905)} = 0.1185$$

(1) + (2) + (3) = 1.0739
$L = 10$ is too low—
Try $L = 15$, then—
(1) + (2) + (3) = .0622 + 0.8662 + .0954 = 1.0238
$L = 15$ is still too low.
Try $L = 18$
(1) + (2) + (3) = .0642 + 0.8480 + .0853 = 0.9975
Interpolating
$1.0238 - .9975 = 0.0263$
$1.0238 - 1.000 = 0.0238$

$$15 + \frac{.0238\ (18 - 15)}{.0263} = 15 + 2.72 = 17.72\%$$

The liquid will amount to 17.72 mol per cent as a first approximation and the uncondensed vapor 82.28 mol per cent by difference.

STEP 3

$$CH_4 = \frac{17.72 \times 43.4}{803 + 17.72\ (-703)} = 1.13 \text{ mols}$$

$$C_2H = \frac{17.72 \times 54.4}{56.3 + 17.72\ (0.437)} = 14.96 \text{ mols}$$

$$C_3H_8 = \frac{17.72 \times 02.2}{9.50 + 17.72\ (0.905)} = 1.53 \text{ mols}$$

or a total of 17.62 mols of liquid as condensate, therefore

$CH_4 = 6.41\%$
$C_2H_6 = 84.90\%$
$C_3H_8 = 8.69\%$

Which is the composition of the condensate.

The composition of the uncondensed vapors may then be calculated by methods previously given. The condensate may be totally returned to the column as reflux or part of it withdrawn from the system. A high reflux ratio would materially reduce the amount of propane in the distillate from the column.

The next step is to remove the propane. The operating pressure to be held on the column will be determined, fixed by the highest temperature of the cooling water available for the condensers unless refrigeration is to be resorted to again. One proceeds as before in calculating the composition of distillate and reflux.

CALCULATION OF LATENT HEAT

The latent heat of vaporization decreases with the pressure on the system. In Chart No. 3 the data from Young's partly experimental values for N-Pentane have been plotted in the form of a curve of latent heat per pound in B.t.u. versus temperature. The temperatures are taken from the vapor pressure curve and correspond to fixed pressures at each point. The values for latent heat in B.t.u. could just as well have been plotted against the corresponding vapor pressures. The dotted portion of the curve is extrapolated but fits in well with the values calculated from the equation:

$$X = \frac{1.985}{M}\left(\frac{T_2\ T_1}{T_2 - T}\right)\left(1 - \frac{P}{P_c}\right) \ln \frac{P_2}{P_1}$$

In Chart No. 4 a few of the unchecked values for latent in B.t.u. per pound have been plotted in the form of uncompleted curves lying within the temperature ranges used in natural gasoline rectification.

In the case of liquid mixtures for which the vapor pressure curves and the analysis are available, the critical pressure is first computed by the equation:

$T = x_1 T^1_c + x_2 T^2_c + x_3 T^3_c$
where T^1_c, T^2_c, T^3_c are the respective critical temperatures in degrees absolute of the components and x_1, x_2, x_3, etc., the respective mol fractions.

The critical pressures for mixtures may be calculated by similar equations using the critical pressures of the components instead of the temperatures. This indirect method seems to offer the only practical means for close approximation of the heat required for mixture vaporization and condensation short of experimental determination which is hopeless because of the endless and ever varying changes in composition. The problem of determining the latent heat is of paramount importance as quantitative mathematical analysis relative to rectification has its basis in heat input and heat abstraction as applies to vaporization and condensation.

PART 2

Gases Produced from Cracking Oil in Vapor Phase

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THROUGH a cooperative arrangement with the Petroleum Division of the American Chemical Society a series of technical articles will be presented in THE REFINER AND NATURAL GASOLINE MANUFACTURER *for distribution in English in this country and abroad. The articles are translated from the Russian by members of the Petroleum Division of the American Chemical Society, thus making available the results of research carried out in the scientific laboratories of the Soviet.*

The accompanying discussion, constituting Part 2 of the first of the series, deals with gases produced by cracking oil in the vapor phase. This gaseous production of vapor phase cracking is one of the richest and most accessible sources of raw material for the synthesis of a very large number of chemical products. The presentation of this work will be concluded in an early issue.

4. QUANTITATIVE CHARACTER OF ISOTHERMAL DISTILLATION OF BLAUGAS FRACTION

THE described method was used to determine relation between the pressure of isothermal vaporization of blaugas fraction[29] (or products of the second distillation) and:

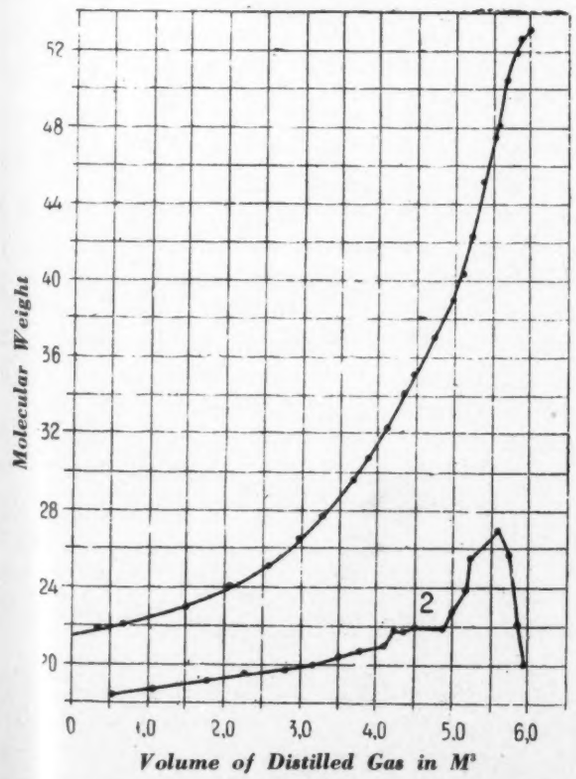
(1) Specific gravity or molecular weight;

(2) Weight of distilled gases;

(3) and composition of distilled gases according to its components, etc.

Of all available figures, we will give only those which are the most complete and distinct in character. First of all we will give figures for the typical case of normal blaugas fraction.

FIGURE NO. 3



Relation Between Molecular Weights and Quantity of Fraction of Isothermally Distilled Wet Gas

1—Curve of average Molecular Weights.
2—Derivative of curve 1.

Fig. 1 gives the relation between the pressure of distillation and average molecular weight based on the specific gravity. We see a complex curve but, in general, sufficiently smooth. However, if we lay out volumes instead of pressures on the abscissa as it is done in Figure No. 3, the picture will be considerably changed.

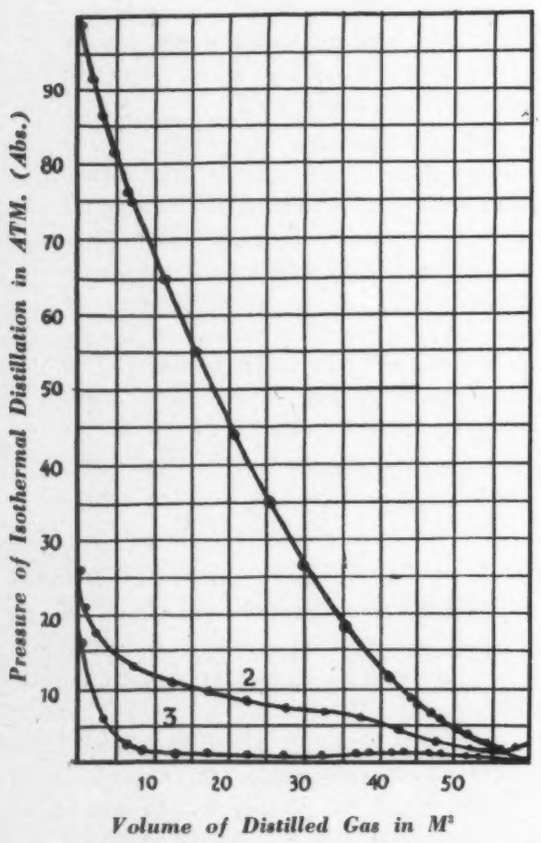
For the first 50% of the volume a constant increase of molecular weight is noted. Further the speed is getting greater, then is slowed down again (so called area of first retardation, or "propylene" see below); after that it increases sharply again to slow down and finally to decrease at the end, (so called area of

the second retardation or "butylene"). These two areas of retardation are of special interest. They are easily seen in the form of horizontal minimums on the curve showing the derivative by volume. The first area of retardation corresponds to molecular weight of 34-33 and second to 46-53.

It is very interesting to note that the molecular weight of the first area, 34-38, approaches that of propylene (42) and that of second (46-53) approaches the mol wt. of butylene (56) or divinyl (54). Strictly speaking, in both cases the quantities of these areas are somewhat smaller than theoretical quantities. This hardly speaks in favor of possible assumption of existance of constantly boiling mixtures here; more probably there is going on a vaporization of propylene in a stream of easier boiling gases dissolved in liquids. The created picture is well correlated with our presumptions of correlation in case of the usual isobaric distillations.

The second feature resulting from the analysis of the figures 1 and 3 is that the slowing down of increasing average molecular weights in the propylene area (34-38) does not entirely correspond to the maximum of the second absorption when comparing the curves given on Fig. No. 7; the first is noticed earlier than the second. The "propylene" area of the curve of molecular weights corresponds to 73-80% on the axis of volumes, or to 9.5 to 6 abs. atm., while the maximum of the second absorber is in the

FIGURE NO. 4



Relation Between Volumes of Distilled Gas and Pressure of Distillation for Wet Gases

1—Curve $F = \frac{\Delta P}{\Delta V}$

2—Curve of the first derivative function $\varphi = \left(\frac{\Delta P}{\Delta V}\right)'$

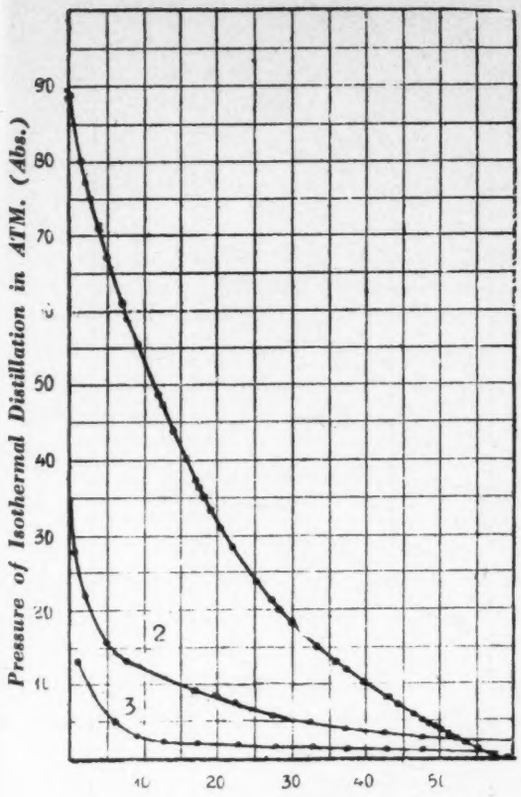
3—Curve of the second derivative function $\Theta = \left(\frac{\Delta P}{\Delta V}\right)''$

TABLE NO. 4

PHYSICAL CHARACTERISTICS OF DISTILLATION

Pressure	Drop in pressure	Sp. wt. of distilled gas	Indicating data of gas meter: At start of distillation	Indicating data of gas meter: Volume of fraction	Indicating data of gas meter: Per cent in respect to total distilled over volume	Weight of distilled over gases	Average Molecular weight of distilled over gas
atm. (absol.)	atm.	15° in respect to air	L		%	Kg	
1	2	3	4	5	6	7	8
99		0.738	....	...	...	...	21.4
	12.5			347			
86.5		0.753	347		6.8	0.36	21.8
	10.5			340			
76			690			0.67	
	1.0						
75		0.761	697			0.71	22.0
	10.0			451			
65		0.766	1148		19.1	1.16	22.2
	10.0			416			
55			1564		26.0	1.60	
	0.5						
54.5		0.788		521		1.01	22.8
	10.0						
44.5			2085		34.4	2.16	
	0.3			15			
44.2		0.899	2100		35		24.0
	9.2			510			
35.0		0.864	2610		43.5	2.72	25.0
				390			
27.5	7.5	0.915	3000			3.18	26.5
20.5			3510		48.5	3.85	
		1.018		190			
16	2.9	1.090	3700		61.5	4.18	29.5
	4.6			410			
12.0	4.0	1.113	4110		68.5		32.2
	0.5						
11.5						4.82	32.5
	2.9	1.123		105	73.5		
8.6		1.202	4415			5.28	34.8
	0.1			20			
8.5		1.202	4435		74	5.42	34.8
	1.9			315			
6.6		1.278	4750		79	5.98	37.0
	0.1			50			
6.5		1.280	4800		80		37.1
	1.3			170			
5.2		1.337	4970		82.7	6.38	38.7
	1.0			150			
4.2		1.388	5120		85.4	6.69	40.2
	0.2						
4.0		1.393					40.4
	0.03			280			
397						6.82	40.4
	1.89						
2.68		1.552	5400		90	7.46	45.0
	0.98			270			
1.70		1.740	5670		94.5	8.10	50.4
	0.45			30			
1.50							
1.25		1.797	5800		96.7		51.8
	0.25			200			
1.00		1.830	6000		100	9.80	53.0

FIGURE NO. 5



Relation Between Volumes of Distilled Gas Pressure of Distillation for Propylene Concentration.

1—Curve $f = \frac{\Delta P}{\Delta V}$

2—Curve of the first derivative function $\varphi = \left(\frac{\Delta P}{\Delta V}\right)'$

3—Curve of the second derivative function of $\Theta = \left(\frac{\Delta P}{\Delta V}\right)''$

area of 88-93% on the axis of volumes or to 3 to 2 abs. atm. It is also true, although to a smaller extent, that the butylene area of the curve of molecular weight begins a little earlier than the sharp increase of the curve of the first absorber. (See Fig. No. 8.) This shows that hydrocarbons with four carbon atoms play a great part in the content of gases absorbed by the second absorber, and that the apex of the curve (Fig. No. 7) is caused by these hydrocarbons; the content of the true propylene probably starts to diminish right after 80% on the axis for volumes. This indirect deduction is proven by actual figures below.

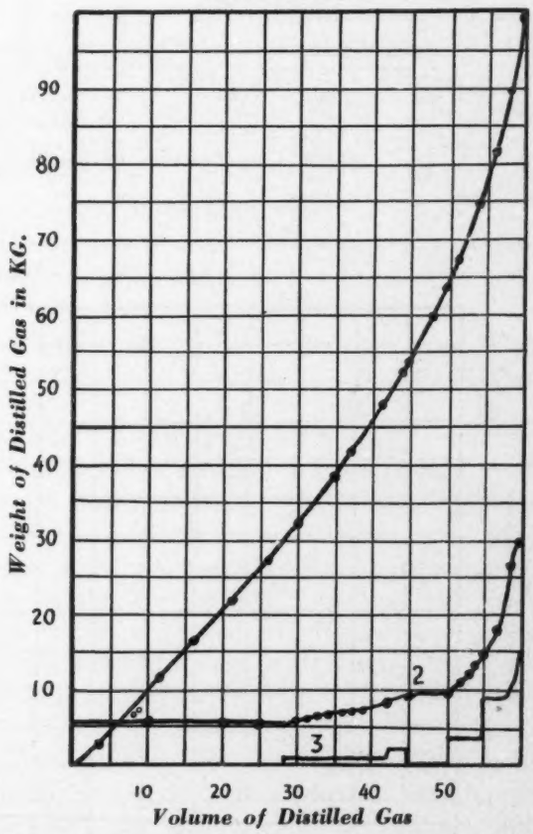
The curves for the relation of pressures to volumes of distilled gases $\frac{\Delta p}{\Delta V}$ (Fig. No. 4) are smooth. Their first derivatives also do not show special areas; the analysis of the second derivatives by volume permits us to say that, with exception of the first portion (first 15 to 20% of volume), this curve can be expressed by one equation of the second degree. This is true of the whole curve with exception of the areas for 20 to 5 atmospheres, where we will get results somewhat lower than those obtained from the experimental determination.

For the second case, namely for the fraction of the propylene concentration of wide ranges (that is for the curve obtained as a result of three distillations) the exceptions from the equation of the second degree are entirely insignificant (see Fig. No. 5).

As we should expect, the relation between the weight and volume of the distilled gas does not give such a binding curve as we got for "pressure and volume" case.

Making the first derivative by volume for a function $\varphi = \left(\frac{\Delta \gamma}{\Delta V}\right)^1$ we will get a picture expressed by line 2 on Fig. No. 6. As it is seen the curve expressing this derivative consists of pieces of straight lines with exception of the last points. The portions of the curve corresponding to: (1) first 50% of volumes (from 100 atm. to 28 atm.) and (2) from 8.5 to 5 atm. are horizontal,—that is for the primary functions $\varphi = \left(\frac{\Delta \gamma}{\Delta V}\right)^1$ are expressed by an equation of the first degree. Second portion is similar to horizontal

FIGURE NO. 6



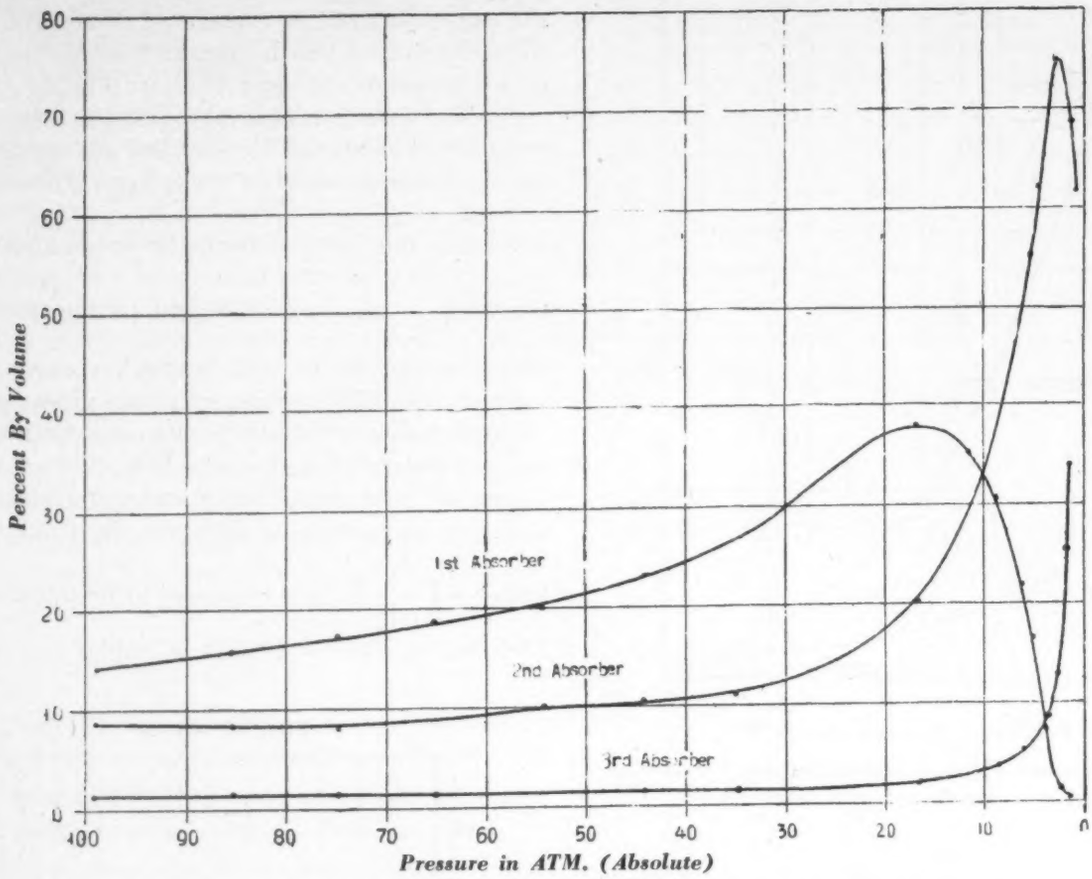
Relation Between Weight and Volume of Distilled Gas

1—Curve $f = \frac{\Delta q}{\Delta V}$

2—Curve of the first derivative function $\varphi = \left(\frac{\Delta q}{\Delta V}\right)'$

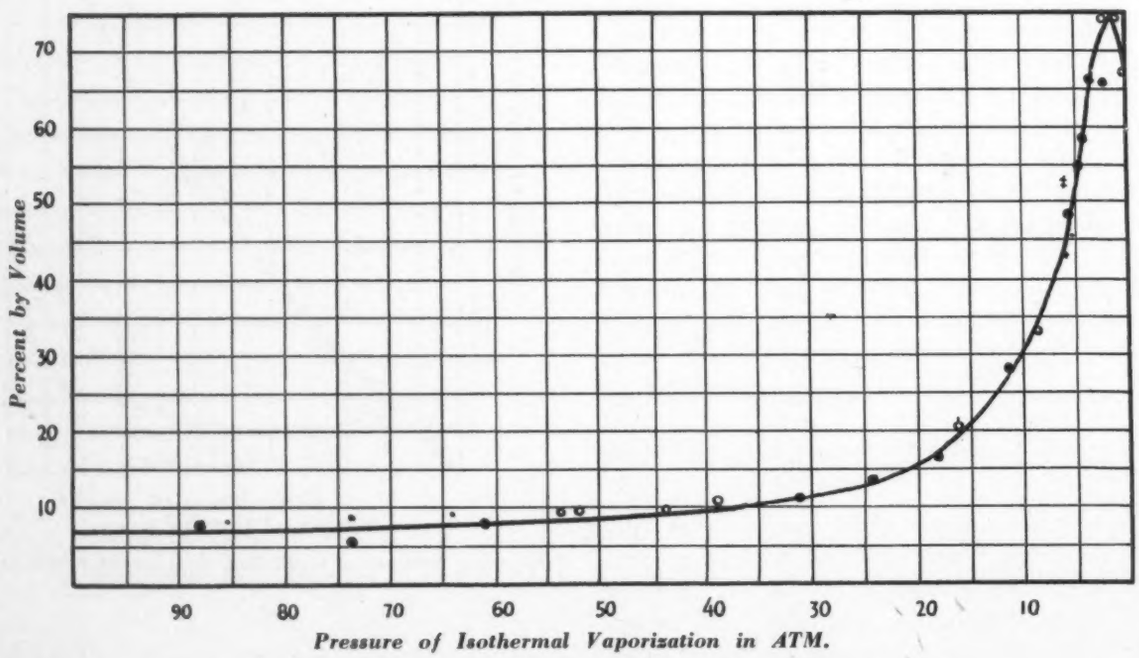
3—Curve of second derivative of function $\Theta = \left(\frac{\Delta q}{\Delta V}\right)''$

FIGURE NO. 7



Analysis of Fraction of Isothermally Distilled Wet Gases for Unsaturates

FIGURE NO. 8



Data of Analysis for Various Products from Second Absorption.

portion of the first derivative "molecular weight to volume" according to its position (see Fig. No. 3). A horizontal portion on the curve $\left(\frac{\Delta \gamma}{\Delta V}\right)^1$ similar to "butylene" portion on the curve $\left(\frac{\Delta m}{\Delta p}\right)^1$ is not existing.

The weight to volume curve can be expressed by a row of equations of second degree with exception of the described portions (from 100 to 28 atm. and from 8.5 to 5 atm.); and these equations, after schemalizing them, will be independent for each of the following portions (reading on the axis for volumes):

(1) from 50% to 70%
(2) from 70% to 75%
(3) from 83% to 92%

Finally the curve from 92% to 100% of volume, that is the last portion, is expressed by an equation of higher degree.

The described analysis of the weight-volume curve is especially visible on the second schematically shown derivation curve—3 on Fig. 6. This line gives valuable indications for organization and performance of the process of distillation of wet gases under the conditions of rectification. (See below.)

Figure No. 7 expresses results of the analysis of the unsaturates of the gas with introduction of correction for extrapolation of the absorption curve for the first and second absorber.

5. CONTENT OF DIVINYL AND METHOD OF DETERMINATION

The determination of divinyl in gases by our method of fractional absorption with H_2SO_4 is impractical according to the above descriptions. At the same time, knowing only the content of divinyl in the gas, we can judge about the quantity of normal butylene, because the described above method can give the total of both of them and only by the indirect calculations. Divinyls are existing mostly in the heavy fractions of gaseous distillation. These fractions are rich in butylenes and vapors of amylenes. In general these heavy fractions can be studied by the above methods only with a comparatively small degree of accuracy. And when dealing with the last gaseous cuts which are being condensed at 0°C, etc., the mistake of determination is more than 2-3% of the whole volume even with introduction of a correction by the method of interpolation.

Usually the determination of divinyl is performed by the method of brominization.

During our investigation we used mostly the common method of determination of divinyl. This method consists of complete brominization of all double bonded unsaturates of standard gases, by passing them through a thick layer of a solution of bromine in C Cl_4 and chloroform at 0°C. The products of brominization are distilled then under vacuum at .15 atm. on a water bath and the residue is considered to consist of tetrobromide (see below).

The process consists of a series of reactions, the result of which often is a formation of mono-and poly-bromides besides dibromides.

Our experiments, and also the collected information, show that the application of brominization for qualitative determination of mono-olefins, particularly butylene, and amylene, do not withstand criticism.

Although this method is not satisfactory for us, there is nothing else to apply for determination of divinyls. It must be admitted that the brominization system is more suitable for determination of divinyls than for butylene, etc. (there is no danger in respect to formation of mono- and tri-bromides; no loss of unstable bromides during distillation, etc.).[30]

Of course the raw tetrabromide, is hardly the only product obtained from divinyls.

To judge about the content of the last in them, a separation of divinyls from the raw tetrabromides is generally done by means of regeneration with zinc dissolved in alcohol. However, even the pure tetrabromides give formation of divinyls not more than 85-90%.[31]

From the quantity of regeneration of divinyls we can obtain the minimum guaranteed figures. But by figuring out the divinyl from the actual weight of

TABLE 5

CHEMICAL ANALYSIS OF GASEOUS DISTILLATES

Pressure in atm (absol.)	Analysis for Unsaturates Absorbers, H_2SO_4 I 63%	II 84%	III 98%	Total of 1&2 in %	Total of Unsaturates by H_2SO_4 Method in %
99	1.0	9.2	14.3	10.2	24.5
86.5	1.6	8.4	15.6	10.0	25.6
76	...	...	...	...	...
75	1.6	8.2	17.1	9.8	26.9
65	1.6	9.0	18.6	10.6	28.3
55	...	...	...	...	...
54.5	1.2	10.2	19.8	11.4	31.2
44.5	...	...	...	...	...
44.2	1.9	10.4	23.0	12.3	35.3
35.0	1.6	11.4	26.2	13.0	39.2
16.6	2.0	20.4	37.6	22.4	60.0
12.0	3.7	30.5	...	34.2	...
11.5	...	...	...	...	...
8.6	4.4	35.2	30.3	39.2	69.5
8.5	...	...	...	...	...
6.6	...	...	...	...	...
6.5	5.4	47.2	21.5	52.6	74.1
5.2	6.0	55.3	16.1	61.3	74.4
4.2	8.8	62.5	9.2	71.3	80.5
4.0	8.4	65.4	8.4	73.7	82.1
3.97	...	...	...	...	...
2.63	12.6	74.7	1.6	87.3	88.9
1.70	25.0	68.8	0.5	93.8	94.3
1.25	33.0	62.0	...	95.0	95.0
1.00	...	...	...	...	...

(1) Analysis of saturates as given above in No. 2 column of No. 1&2 tables.

TABLE NO. 6

CONTENT OF DIVINYL, OBTAINED BY BROMINIZATION OF HEAVY FRACTIONS

I Series of Experiments

Pressure of Isothermal Distillation in atm (absol.)	Sp. Gravity	Average Molecular Weight of gaseous fractions	Composition by H_2SO_4 Method with extrapolation in %				For the first 1 gas is obtained		Temperature of melting of "cake"	Relation of weight of liquid dist. bromides to the weight of the "cake" (taken as one)	Content of Divinyls			
											I (maximum)		II (minimum)	
			I Absorber	II Absorber	III Absorber	Total of Unsaturates	Bromides total "g"	Cake "g" Included			In gas, g	By volume in %	In gas, g	By volume in %
4.0	1.47	42.5	8.4	65.4	8.4	82.1	6.54	0.74	83°	7.8	0.11	4.6	0.09	3.8
2.7	1.65	48	12.6	74.7	1.6	88.9	7.5	1.00	89°	6.5	0.15	6.0	0.125	5.0
1.7	1.73	50	25.0	69.0	0.5	94.5	9.5	2.6	93°	2.3	0.36	14.9	0.26	12.4
II Series of Experiments														
3.8—2.8	1.52	44	12.0	71	4.0	87.0	6.4	0.9	99°	6.1	0.13	5.4	0.11	4.5
2.7—2.2	1.62	47	13.5	74	2.3	89.8	7.0	1.1	94°	5.4	0.16	5.6	0.13	5.5
1.9—1.4	1.72	50	25	70.5	0.5	91.0	6.7	1.5	94°	3.5	0.22	9.1	0.18	7.7
1.4—1.2	1.79	52	33	61	0	94	5.9	1.9	102°	2.7	0.26	10.8	0.22	9.0
1.2—1.0	1.86	54	37	55	0	92	5.3	1.4	103°	2.8	0.20	8.3	0.17	6.9

See Division IV.

the "cake", we get the maximum content of divinyl. The actual quantity is somewhere between these two figures.

The regeneration of our "cakes" gives us an average of about 76% for divinyls. In the Table No. 6 we give two columns with figures for divinyls. The first row of figures is obtained from the supposition that the "cake" consists of divinyls transferred into tetrabromides. The second row gives figures with a correction for the found averages for regeneration of divinyls from our raw tetrabromides with Thale's information co-efficient (90%).

Data from distillation of two wet gases of two different grades are included in Table No. 6.

Out of the two methods of analysis of divinyls the most adaptable is the A. F. Dobriansky's method,[32] based on the determination of the quantity of double bonded unsaturates in the given gas and comparison of results with theoretical figures, assuming that all unsaturated components of the given gas are mono-olefins.

However, for heavy cuts containing vapors of amylenes, etc., this method does not always give sufficiently good results. In some cases (evidently, this is in connection with the presence of molecules with three, five or more atoms of carbon; however, we can not give any logical reason for it), but not always, low and even negative results are obtained. If we first isolate these hydrocarbons with Jempel's pipet or with the Orse's Type Absorber with 55-60% H_2SO_4, the number of cases with negative results are decreased.

Comparatively good results are obtained during the analysis of highly rectified butylene—divinyl distillation. We have to admit that we did not quite get this method. For this reason we do not believe it is worthwhile to publish the results of our work dealing with products of gaseous distillation of blaugas with a high concentration of divinyls.

[28]Gurvich "Scientific Foundation of Refinery Mineral Oil" page 297.

[29]Pressure in isothermal distillation is identical to temperature in normal isobaric distillation.

[30]A simpler method is entirely adaptable for fractionation of gases having no hydrocarbons with five carbon atoms—see below.

[31]Thiele "Ann" 308, 377, 1899.